STUDIES IN LUMINESCENCE

BY

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PREFACE.

The series of investigations described in this memoir was begun in 1903. The authors believed that by the use of quantitative methods and particularly by the application of the spectrophotometer to the study of the spectra of fluorescent and phosphorescent substances, something of definite value might be added to the existing information concerning luminescence.

Spectroscopy, whether visual or photographic, is a method of high precision where applied to line spectra, but in the case of the broad bands of the spectra of fluorescent solids and liquids it affords but little information beyond the approximate width and general location of the bands. The spectrophotometer, on the other hand, enables the observer to determine the distribution of intensities throughout the emission bands and the coefficients of absorption for the various wave-lengths of the corresponding absorption bands. From the curves expressing the results of such measurements, moreover, it is possible to locate with considerable accuracy the crests of the bands. One may thus attain some detailed knowledge of the laws of the radiation of luminescence, compare luminescence with the radiation due to temperature, and obtain a basis for theoretical discussion.

A number of important portions of the work described in this volume have been carried out at our suggestion by Doctors Frances G. Wick, C. A. Pierce, Percy Hodge, and C. W. Waggoner, and by Messrs. H. E. Howe and Carl Zeller. To these investigators and also to Prof. W. R. Orndorff, who has repeatedly aided us by undertaking the preparation of fluorescent compounds and by suggestions concerning the chemical aspects of the problem, we desire to express our indebtedness.

The recent exhaustive, thorough, and discriminating review of the very large literature relating to luminescence published by Professor Kayser (H. Kayser, Handbuch der Spektroskopie, Bd. IV, Kap. V and VI) in his Handbook of Spectroscopy, makes any extended bibliographic or historic treatment here unnecessary and we have therefore given only such references to previous researches as bear directly upon the subjects under consideration.

The subject-matter contained in the several chapters appeared from time to time, as each portion of the work reached completion, in a series of papers in the Physical Review. In gathering this material together in a single treatise we have recast and rearranged it, but have preserved the original form of presentation in so far as it was found to be consistent with our views after the completion of the work.

Grants which were received from the Carnegie Institution of Washington in 1905, 1909, and 1910 have greatly facilitated the prosecution of the experiments described in this memoir and of others now in progress and have furthered the preparation for investigations which it is proposed to undertake in the near future.

Physics Laboratory of Cornell University,
May 23, 1911.

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CHAPTER I.

A SPECTROPHOTOMETRIC STUDY OF FLUORESCENCE.[1]

The law expressed by Stokes[2] in his memoir entitled "The Change of Refrangibility of Light," to the effect that in fluorescence the fluorescent light is always of greater wave-length than the exciting light, has been called in question by Lommel, who pointed out that for certain fluorescent bodies there is an unmistakable overlapping of the regions in the spectrum occupied by the exciting light and by the fluorescence which it produces. Lommel made the further very important statement that for this class of substances the character and composition of the fluorescence spectrum are independent of the wave-length of the exciting light. Lommel's results, in so far as they had to do with the non-validity of Stokes's law, were confirmed by Hagenbach.[3] A few years later Lubarsch[4] published measurements in confirmation of Stokes's law. A later paper by Lommel,[5] in which he described the fluorescence of the so-called chameleon colors, led Hagenbach to new experiments, in the course of which he discovered what he believed to be a source of error in his former measurements, and he reaffirmed the law of Stokes for all such substances. In 1877, Brauner[6] obtained results in confirmation of Lommel's view. In 1879, Lubarsch[7] published further experiments on fluorescence, this time in favor of Lommel's results. Lamansky[8] in 1879 described measurements in confirmation of Stokes's law. In a still later paper Hagenbach[9] returned to the defense of Stokes's law as against Lommel[10] and Lubarsch,[11] who in the meantime had published further articles dealing with his objections and criticizing Lamansky's method. Wesendonck[12] in 1885 made observations with the sun's spectrum, using two concave mirrors and a prism, in the course of which he obtained conclusive evidence that the fluorescence of naphthalin-roth extended to wave-lengths shorter than that of the exciting light. In 1886, Stenger[13] took the question up at length. He found that whether he used Hagenbach's method of illuminating the free surface, Lommel's method of grazing incidence through the side of a flask, or Lubarsch's fluorescent eye-piece, his measurements confirmed Lommel as to the invalidity of Stokes's law but not as to the independence of the fluorescent spectrum from the character of the exciting light. He also made experiments in collaboration with Hagenbach, who was finally converted to the same view.

It is our purpose in this chapter to describe results obtained by the application of the spectrophotometer to the measurement of the fluorescence spectrum of those substances concerning the fluorescence of

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[1] Physical Review, xviii, p. 403, and xix, p. 18.
[2] Stokes, Phil. Trans., p. 463, 1852.
[3] Hagenbach, Poggendorff's Ann., 146, pp. 65, 232, 373, 508.
[4] Lubarsch, Poggendorff's Ann., 153, p. 428, 1874.
[5] Lommel, Poggendorff's Ann., 159, p. 514, 1876.
[6] Brauner, Wiener Anzeiger, 19, p. 178, 1877.
[7] Lubarsch, Wied. Ann., 6, p. 248.
[8] Lamansky, Comptes Rendus, 88, p. 1192, 1879.
[9] Hagenbach, Wied. Ann., 18, p. 45.
[10] Lommel, Wied. Ann., 8, p. 244, 1879.
[11] Lubarsch, Wied. Ann., 9, p. 665, 1980; also Wied. Ann., 11, p. 68, 1880.
[12] Wesendonck, Wied. Ann., 26, p. 521, 1885.
[13] Stenger, Wied. Ann., 28, p. 201.

which, especially with reference to the validity of Stokes's law, the long-continued discussion already described arose. But few attempts have been made to apply the spectrophotometer to the study of fluorescence; yet it is obviously possible to determine both the limits and the maximum of a spectral region for which a curve of intensities can be plotted with far greater accuracy than by the method hitherto pursued by all observers, *i. e.*, that of attempting to set the cross-hair in the eye-piece of a spectroscope in the region of greatest brightness, or at the point where the spectrum ceases to be visible. Experimenters have perhaps been deterred from the use of the spectrophotometer because of the faintness of fluorescence spectra. It is true that the fluorescent light from many substances is so weak as to preclude all measurements of its spectrum; but it is also true, as we have found in the course of the experiments to be described, that settings can be made in cases where the brightness of the spectrum is far below that necessary to arouse the sense of color and where the presence of light can be detected only after prolonged shielding of the eye. The use of the cross-hair in such cases is out of the question, for the field is much too dim to render it visible, while every attempt to illuminate it from the side would flood the eye-piece with light sufficient to quench that under observation.

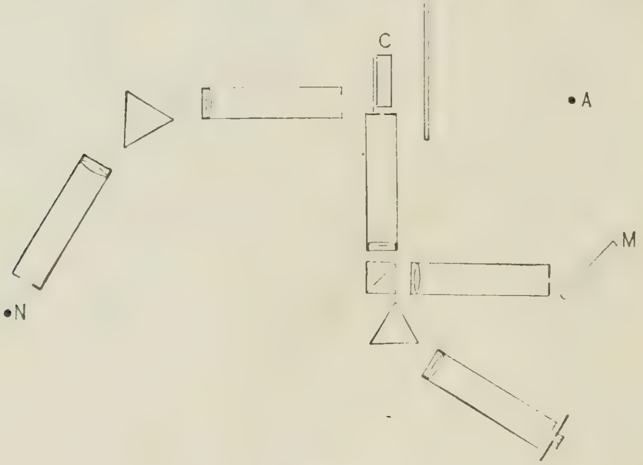

Fig. 1.

The instrument used in most of our observations was the spectrophotometer of Lummer and Brodhun. In many of our earlier measurements the ocular lenses in the eye-piece were used, the eye being focused upon the aperture in the eye-piece and not upon the face of the prism. By means of metal screens attached to the collimator slits of the instrument the length of slit was regulated so as to avoid overlapping of the spectral images and to give two contiguous spectra in the field of view. One loses in this way the advantage of the method of contrast, but the brightness of the field is greatly increased. Later on the contrast field was employed because it was found to be less fatiguing to the eye and on the whole more accurate. Since in most cases it was desired to employ monochromatic light for the excitation of fluorescence, the spectrophotometer was employed in connection with a large spectrometer, as shown in Fig. 1. The eye-piece and slit of the spectrometer were removed, and in place of the latter a Nernst filament (*N*) was mounted vertically. This filament afforded a nearly linear source of light, giving a sufficiently powerful continuous spectrum. The filament was attached to the arm carrying the collimator tube so as to move with the latter and to remain in the vertical plane passing through its axis. The observing telescope was clamped, and different portions of the spectrum were brought into the field as desired by movements of the collimator tube. The liquid, the fluorescence of which was to be studied, was placed in a rectangular cell (*C*), upon one face of which a real image of the spectrum was focused. This face of the cell was provided with a metal screen having a vertical opening 1 mm. wide, through which the light used for exciting fluorescence could pass. This opening (see Fig. 2) was so placed that the exciting light entering the cell would be parallel to the adjacent face of the cell and as near to the same as practicable. In adjusting the metal screen one edge of the slit or opening was made to exactly cover the glass forming this face of the cell, as shown in the figure. The fluorescence spectrum was observed from a direction at right angles to the path of the exciting beam, and in order to bring the brightest fluorescence regions of the liquid into the field the vertical plane of the collimator of the spectrophotometer was adjusted so as to bring into the field of view the layer of liquid lying next to the face of the cell through which the exciting light entered. By this arrangement the width of the opening through which the light entered the cell and the width of the slit of the spectrophotometer each being 1 mm., the average depth of liquid within which fluorescence was produced was approximately 0.55 mm. and the average distance which the fluorescence light passed through the liquid before leaving the cell was also 0.55 mm.

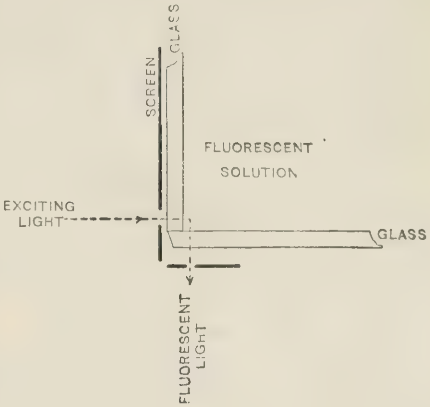

Fig. 2.

The source, *A*, of the comparison spectrum (Fig. 1) was an acetylene flame, the light from which was reflected diffusely from the face of the block of magnesium carbonate (*M*) mounted at an angle of 45° at the end of the collimator slit. Measurements were made by varying the width of the slit until the two regions of the spectrum under observation were equally bright.

The substances specified by Lommel as belonging to his first class, in which it is possible to excite fluorescence by means of light of wave-length longer than that of a portion of the fluorescence spectrum, and in which the distribution of intensities in the fluorescence spectrum is independent of the character of the exciting light, are *naphthalin-roth*, *eosin*, and *chlorophyll*. To this list Stenger added the substance *fluorescein*. The last-named substance, on account of its intense fluorescence and the location of the fluorescent band in the middle of the spectrum, in the regions of the highest luminosity, was selected for detailed study for the purpose of testing the conclusions reached by Lommel and the other investigators mentioned in the opening paragraphs of this chapter.

Ten cubic centimeters of alcohol were saturated with fluorescein at room temperature and the solution was filtered. To 40 c. c. of distilled water one drop of a normal solution of sodium carbonate (Na_2CO_3) was added. Two parts of the concentrated alcoholic solution were then mixed with 100 parts of the water thus rendered alkaline. The fluorescence spectrum of this solution, excited by the undispersed rays of the acetylene flame, was first measured, the distribution of intensities being compared, as in nearly all our subsequent experiments, with the spectrum of the light diffusely reflected from the surface of the block of magnesium carbonate shown in Fig. 1. The absorption spectrum of the solution was then taken, the transmission through the cell, which had a thickness of 1.1 cm., being measured by means of the spectrophotometer. The source of the transmitted light was a second similar block of magnesium carbonate illuminated by the same acetylene flame that served for the comparison spectrum.

Much stress having been laid by some of the previous observers upon the influence of stray light, the following measurements were made. The cell was filled with distilled water, set up precisely in the position in which it had been placed in the study of the fluorescence spectrum, and similarly illuminated by means of the acetylene flame. No measurable stray light was found, but an exceedingly weak fluorescence spectrum due to the glass walls of the cell was detected. Since the maximum of the fluorescence spectrum of the glass was found to lie further to the violet than the fluorescence spectrum of the fluorescein, and since moreover it was of scarcely measurable intensity, it was not deemed necessary to take further cognizance of these sources of error.

To determine the fluorescence spectrum of the solution when excited by monochromatic light, a mercury arc-light of the Lummer pattern was used for excitation. It was found that the violet lines from the spectrum of this arc produced fluorescence corresponding, as regards the position of the maximum and the general form, with the curve previously obtained by means of the light of the acetylene flame, but that the green line ($\lambda = 0.575$) excited no fluorescence. This latter result was to be expected, since this line lies altogether outside of the absorption band of the solution in a region for which almost complete transparency exists. The spectrum of the acetylene flame was subsequently tried as an exciting source, but it was too weak to give easily measurable intensities of fluorescence. The slit of the spectrometer was then removed and a Nernst filament, N, was mounted in the axis of the collimator tube as shown in Fig. 1. This filament was found to be of abundant brilliancy. It was maintained at constant brightness by means of a variable resistance, which was adjusted whenever the fluctuations of an ammeter placed in the electric circuit indicated it to be necessary.

Measurements of the fluorescence spectrum of the solution were made by means of the spectrum of the Nernst filament, using as exciting light three nearly monochromatic regions of wave-length, $\lambda = 0.518\,\mu$ to $0.536\,\mu$, $\lambda = 0.487\,\mu$ to $0.502\,\mu$ and $\lambda = 0.460\,\mu$ to $0.471\,\mu$. The curves thus obtained are plotted in Fig. 3, together with the curve of transmission for the solution. It will be seen from this figure that the maximum of intensity of the fluorescence spectrum in these three cases lies in the same region, at 0.517 μ, and that there is no evidence of any shifting of the fluorescence spectrum with the wave-length of the exciting light. It is obvious, moreover, that not only is it possible in the case of this solution to obtain fluorescence of refrangibility greater than that of the exciting light, but that in the case of the curve marked *A* the maximum of the fluorescence spectrum is of shorter wave-length than the shortest wave-length used in excitation. These curves likewise agree fully in character, and as regards the position of their maximum, with that for the fluorescence spectrum of the same solution when excited by the undispersed light of the acetylene flame. (Not shown in the figure.)

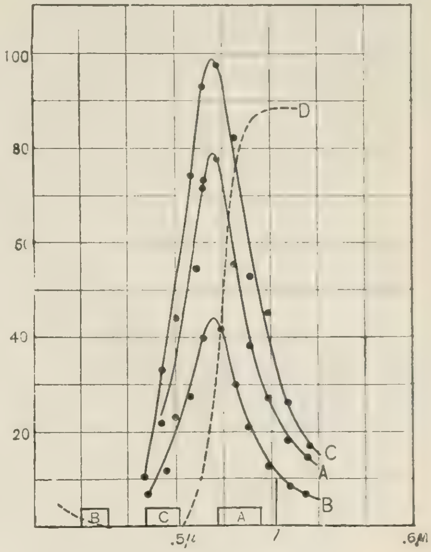

Fig. 3.—Fluorescein.

Fluorescence spectra obtained when the exciting light lies in different regions of the spectrum. For curve *A*, the exciting light was confined to the region marked *A* on the horizontal axis, etc. Vertical scales arbitrary.

These curves for the fluorescence spectrum do not correspond precisely with the typical curve, meaning by that term the curve representing the distribution of intensities in the fluorescence spectrum of the surface layer of the fluorescing liquid. It is possible, however, in the case of a non-turbid medium, to compute from the observed curve the approximate form of the typical curve. Fig. 4 shows graphically the result of such a computation.[1] Curve *A* gives the transmission of a glass cell containing a layer 1.1 cm. in thickness of the fluorescein solution. The dotted curve of similar form gives the transmission corrected for losses in the cell when filled with distilled water. From this, by the well-known law of variation of absorption with the thickness, the curve *D* is found for a layer 0.055 cm. in thickness, which is the estimated mean distance through the solution which the fluorescent light passes before entering the slit of the spectrophotometer. The curve *B* is the observed curve of the distribution of the intensities in the fluorescence spectrum, and from this was computed the curve *E*, which represents, as nearly as the accuracy of the data will allow, the typical curve for this substance, corrected for absorption. It will be seen that in the case of this solution, under the conditions of the measurements, the absorption of the fluorescent light by the solution produces only a slight shift of the maximum toward the longer wave-lengths. When the fluorescent light passes through a considerable layer of the solution the effect of absorption is much more marked and there is a decided change of color. When a thin

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[1] In this figure and in Figs. 5, 6, 7, and 8 the scale of wave-lengths has been doubled.

layer of the solution of fluorescein is viewed by reflected light its color is green, whereas the fluorescence of a mass of the liquid appears decidedly yellowish. This change is shown graphically in the curves of Fig. 5. In this figure *A* is the transmission curve of the solution; *B* is the observed curve of fluorescence when the slit through which the excited light enters the cell is placed so that the fluorescent light passes through 0.055 cm. of the solution before exit; and *C* is the fluorescence curve when the slit is shifted to such a position that the fluorescent light passes through 1 cm. of the solu-

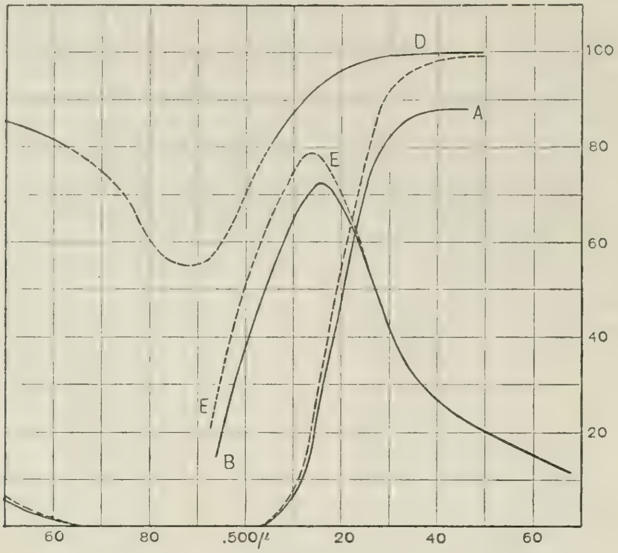

Fig. 4.—Fluorescein.
Typical fluorescence spectrum (*EE*).

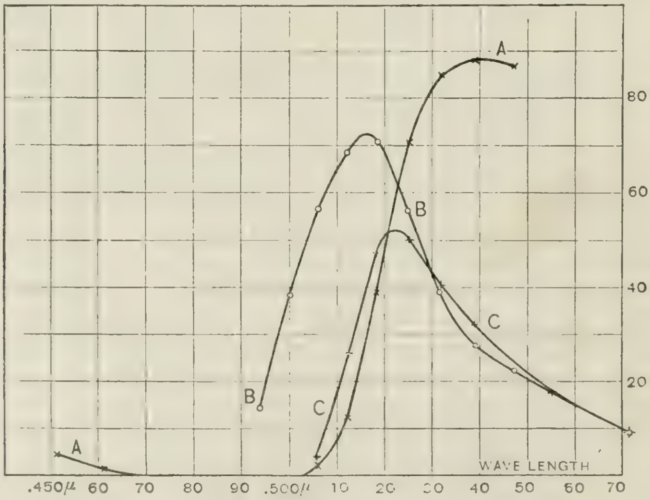

Fig. 5.—Fluorescein.
Effect of absorption upon the fluorescence spectrum.

tion. It will be seen that the maximum is shifted from 0.516 μ to 0.522 μ, and that while the two curves are nearly coincident on the side toward the red the values on the other side of the curve fall off very rapidly as the result of the increased absorption. The boundary of the fluorescence spectrum toward the violet in the one case would lie at about wave-length 0.505 μ, whereas in the thinner layer it would be visible to at least 0.490 μ. It is obvious that the color of the fluorescence in the latter case will contain a great excess of green.

The effect of diluting the fluorescent solution is similar to that of diminishing the distance through which the light passes. The results of observation upon a solution of fluorescein, diluted until the intensity of the fluorescence spectrum was diminished as far as would permit of satisfactory readings, are shown in Fig. 6. The curve *AA* represents the transmission of the cell filled with the dilute solution and *BB* is the distribution curve of its fluorescence spectrum. The dotted lines show the corresponding transmission curve and a portion of the fluorescence curve for the solution before dilution. It will be noted that in this case, as in the case of the comparison of thick and thin layers of a given solution, the curves are coincident toward the red, but that the dilute solution has its maximum shifted toward the green, also that the ordinates on this side of the curve show an increase indicative of the change of color, which, as is well known, is always observed as the result of diluting the fluorescent solutions of this substance.

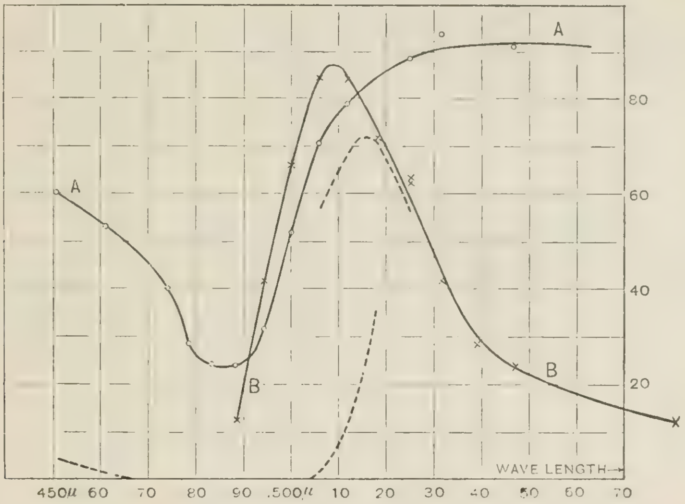

Fig. 6.—Fluorescein.
Effect of dilution upon the fluorescence spectrum.

Although, as has been shown in Figs. 4 and 5, the modifications produced by absorption in the curves of the fluorescence spectrum may be very marked, the effect of absorption diminishes rapidly with dilution of the solution. For example, if we apply the correction for absorption to the curve for the dilute solution in Fig. 6 we find, as is indicated in Fig. 7, that the change is insignificant. In this figure *C* is the observed curve for the fluorescence of the dilute solution, *A* the transmission curve of a layer 1.1 cm. in thickness, and *B* the computed curve for the transmission of the mean layer of liquid through which the fluorescent light has to pass. The correction for this absorption is indicated by means of the dotted line.

It having been established that the fluorescence of bodies of this class is independent, as regards the distribution of intensities, of the wave-length of the exciting source, it would be of interest to inquire whether the fluorescent energy for a given wave-length of the fluorescence spectrum varies with the wave-length of the exciting light when the energy of the latter is constant, or whether it depends only upon the energy. The rigorous determination of these relations involves a knowledge of the distribution of energy in the spectrum of the exciting source, a difficult matter to determine with accuracy for the shorter wave-lengths of the visible spectrum. The curve which is shown in Fig. 8 may, however, be of some interest in this connection. It represents the intensity of fluorescence, taken at the maximum of the fluorescence spectrum of the solution of fluorescein, as a function of the wave-length of the exciting light. Curve *A* was taken with the Nernst filament as a source, curve *B* with the acetylene flame. The dotted line shows the absorption band for a layer of the solution 1.1 cm. thick. It will be seen that fluorescence begins approximately at the wave-length at which the solution begins to absorb, and that the maximum lies well within the absorption band but is shifted to the red. The longer wave-lengths within the band are more effective on account of their greater energy. The difference in the form of the curves *A* and *B* is probably ascribable to the different distributions of energy in the spectra of the sources of light employed. The important questions of the actual distribution of energy in fluorescence spectra and of the relative effectiveness of equal quantities of energy when the wave-length is varied, in producing excitation, are considered at length in Chapters XII and XIII of this memoir.

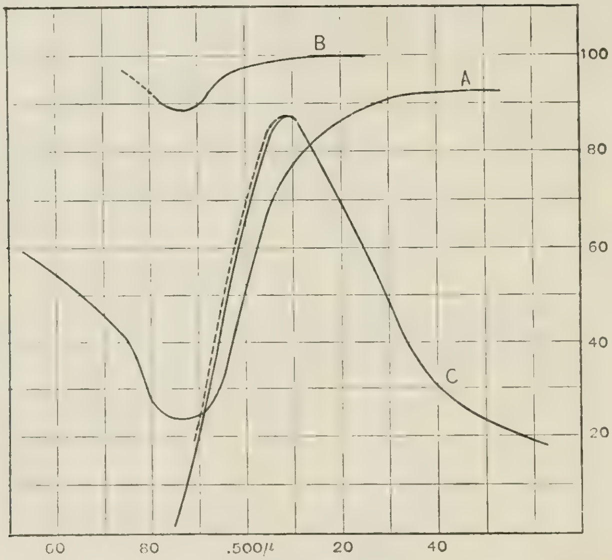

Fig. 7.—Fluorescein.

Typical fluorescence spectrum for dilute solution.

In addition to the measurements on fluorescein the fluorescence spectra of solutions of eosin and naphthalin-roth were also studied by the method already described, and the transmission curves of the solutions were taken.

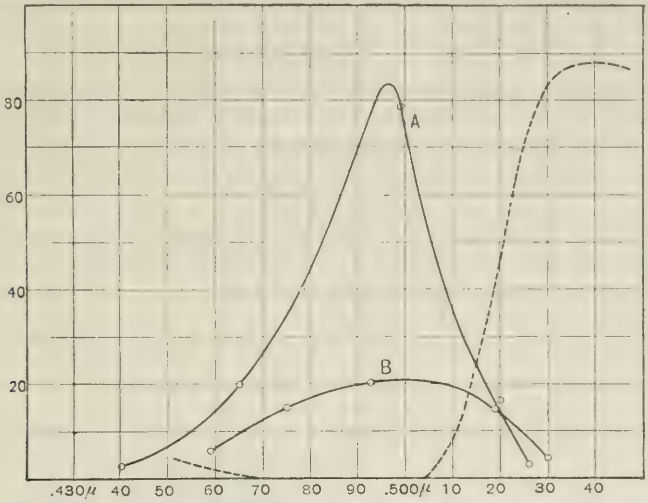

Fig. 8.—Fluorescein.

Intensity of fluorescence as a function of wave-length of exciting light. Ordinates give the intensity of luminescence and abscissas the wave-length of the exciting light. *A* refers to Nernst glower as source, *B* to acetylene flame.

Dilute solutions in alcohol were made, that of the naphthalin-roth being about $\frac{1}{200}$ saturated. The results obtained with these solutions, which are shown in Figs. 9 and 10, afford additional corroboration of the statements

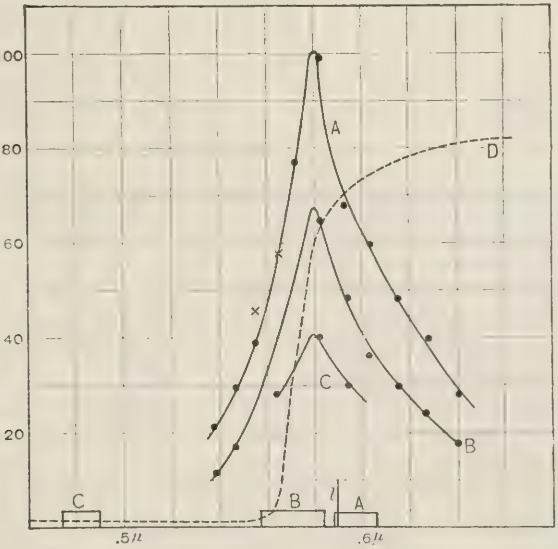

Fig. 9.—Eosin.

Fluorescence spectra observed when the exciting light lies in different regions of the spectrum. Curve *A* was obtained when the exciting light was confined to the region marked *A* on the axis of wave-lengths, etc. Vertical scales arbitrary.

of Lommel. They are indeed in every respect analogous to those obtained with fluorescein and lead to the same conclusions. Each solution was excited by three distinct regions of the spectrum, one lying as far toward the red as practicable, one toward the blue, and one at an intermediate wave-length. Curves showing the distribution of intensities in the three spectra thus produced are shown in the figures and it will be noted that, as in the corresponding curves for fluorescein, the position of the maximum is entirely independent of the wave-length of the exciting light and that the general character of the curve remains unchanged. In the case of these two solutions, as in that of fluorescein, it was possible to obtain a measurable amount of fluorescence by the use of light of wave-length greater than that of the maximum of the fluorescence spectrum. The form of fluorescence curve is very similar for these three substances, but each has its own place in the spectrum. The maximum for fluorescein (Fig. 3) is at 0.517 μ, that for eosin at 0.580 μ, and that for naphthalin-roth at 0.594 μ. The position of the maximum of these three curves with reference to the absorption band appears to vary with the different substances. The maximum for eosin coincides approximately with the infra edge of the absorption band; that for fluorescein lies slightly (about 0.05 μ) toward the violet, while the maximum for naphthalin-roth is much farther displaced toward the short wave-lengths.

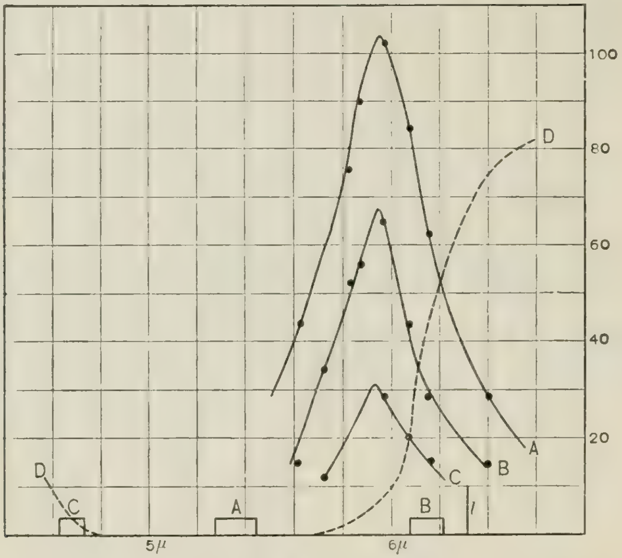

Fig. 10.—Naphthalin-roth.

Fluorescence spectra observed when the exciting light lies in different regions of the spectrum. Curve *A* was obtained when the exciting light was confined to the region marked *A*, etc. Vertical scales arbitrary.

Lommel's contention that it is possible to excite fluorescence in eosin by means of the light of the sodium flame is fully confirmed by the data plotted in Fig. 9, from which it will be seen that the exciting light by means of which curve *A* was obtained had a mean wave-length almost precisely equal to that of the sodium lines. Since it was found possible by means of light, all of which was of greater wave-length than the maximum of the fluorescence spectrum, to produce fluorescence of sufficient strength for measurement with the spectrophotometer, it follows that *observable* fluorescence can be produced by light of even greater wave-length than that recorded in our diagram.

We deem the evidence already given in the foregoing paragraphs to be conclusive, so far as these substances are concerned; but in view of the differences of opinion among physicists as regards the validity of Stokes's law we venture to add the following description of a determination of the wave-length of the least refrangible monochromatic light which we found capable of exciting fluorescence in the three solutions with which this chapter deals.

To insure freedom from the existence of possible errors due to stray light, two different methods were employed of avoiding it. In the first the exciting light, before dispersion, was passed through a solution of the substance to be examined, thus filtering out those rays particularly active in producing fluorescence. The filtered light was then dispersed by means of the large spectroscope already described, and a second solution was subjected to an isolated, nearly monochromatic, region of the spectrum. The wave-length of this region was increased until the last trace of fluorescence, observed directly with the eye, was about to disappear. To distinguish between fluorescence and the presence of light diffused from small particles, the light was viewed at an angle of 90° through a Nicol prism, by which means diffuse light was completely excluded. The limit of excitation thus determined lay, as had been anticipated, farther to the red than in the cases where a *spectrophotometrically measurable* fluorescence had been obtained, excepting in the case of eosin, where it was found to coincide almost exactly with the ultra edge of the band used in exciting the spectrum shown in curve *A* (Fig. 9).

TABLE 1.

Substance.	Maximum wave-length exciting observable fluorescence.
Fluorescein	0.542
Eosin	0.589
Naphthalin-roth	0.632

The second method consisted in sending the isolated region of the dispersed light to be used for excitation through a second spectroscope and determining as before the limit of excitability. This method of removing stray light has been extensively used and is well known to be effectual. The source of light in both cases was an electric arc.

The results obtained by these two methods were identical and are shown in Table 1.

These wave-lengths, all of which lie far to the red from the maximum of the fluorescence spectrum, are indicated in Figs. 3, 8, and 9 by means of the vertical lines marked *l*.

The results obtained with solutions of fluorescein, eosin, and naphthalin-roth thus fully confirm the contention of Lommel[1] that in the case of these substances Stokes's law is not fulfilled. In the opinion of Lommel all other fluorescent substances, with the probable exception of chlorophyll, conform to Stokes's law, the shortest wave-length of the fluorescence spectrum being

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[1] Lommel, Poggendorff's Ann., 143, 159, and 160.

always of less refrangibility than the longest wave-length capable of exciting fluorescence. We later extended our measurements to various other fluorescent substances, determining in each case the location and character of the absorption band with which fluorescence is associated and the form of the curve of relative intensities in the fluorescence spectrum.

RHODAMIN AND RESORCIN-BLAU.

Of the substances examined rhodamin and resorcin-blau belong to the same group as those previously examined, being organic dye-stuffs which show fluorescence in solution. The fluorescence of these solutions was of sufficient intensity to permit of the use of the method already described. Two nearly monochromatic regions of the spectrum were selected in each case, one lying well within the absorption band of the solution and the other as far toward the red as it was possible to go without reducing fluorescence to an extent which rendered measurements inexact. The fluorescence spectrum was observed as before by means of a Lummer-Brodhun spectrophotometer from a direction at right angles to that of the exciting ray. The solution was placed in a glass cell with plane faces, the exciting light being introduced through a slit and passing through the layer of liquid lying next to the wall of the cell through which the fluorescent light passed.

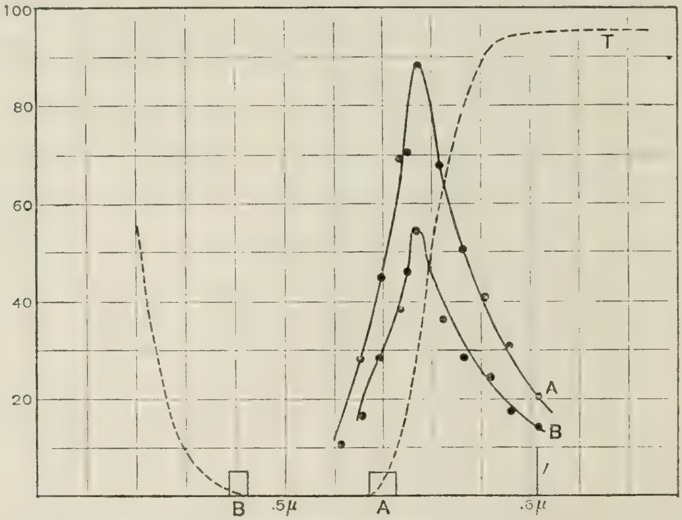

Fig. 11.—Rhodamin.

Curve *A*. Fluorescence spectrum when excited by green light in region marked A.
Curve *B*. Fluorescence spectrum when excited by blue light in region marked B.
Curve *T*. Transmission spectrum. Layer 1.1 cm. thick.

Figures 11 and 12 give in graphical form the results of these measurements. The curves of the fluorescence spectra are of the same type as those of fluorescein, eosin, and naphthalin-roth already cited. They rise from within the region of the absorption band to a well-defined maximum, which is located, generally speaking, near the infra edge of the absorption band; beyond the maximum they fall away rapidly with increasing wave-length. The comparison spectrum in these, as in the previous cases, was that obtained from the light diffusely reflected by a block of magnesium carbonate illuminated by an acetylene flame.

Neither of these solutions conforms even approximately with the law of Stokes. Curve *A* of Fig. 12 (resorcin-blau) was obtained by means of light none of which was of shorter wave-length than 0.642 μ, whereas the fluorescence is of measurable intensity to 600 μ. The rhodamin solution affords a striking example of the non-validity of the law; for although the *maximum* of the fluorescent spectrum lies at 0.554 μ, an observable fluorescence was produced by means of very nearly monochromatic light, obtained by the method of double dispersion, using two spectrometers in series, the shortest wave-length of which was 0.602 μ. This limiting wave-length is indicated by the line marked *l* in Fig. 11. This substance, like eosin, which has its maximum of fluorescence at 0.580 μ, will respond to the excitation of light of the *D* lines of sodium or to even longer waves if of sufficient intensity.

The other substances to be considered in this chapter are more difficult subjects for quantitative work because, being less strongly fluorescent, it is necessary to have recourse to powerful illumination, and because in several instances the fluorescence band lies near the limits of the visible spectrum—either in the violet or in the extreme red.

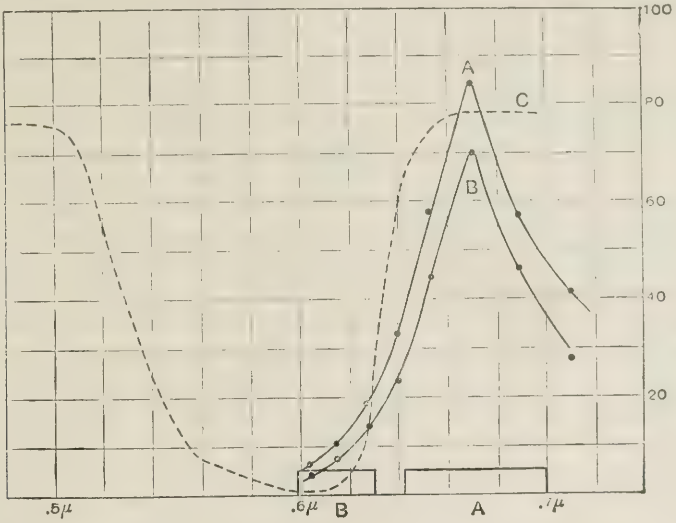

Fig. 12.—Resorcin-blau in methyl alcohol.

Curve *A*. Fluorescence spectrum when excited by red light lying in region marked A.
Curve *B*. Fluorescence spectrum when excited by orange light in region marked B.
Curve *C*. Transmission spectrum of layer 1.1 cm. thick.

QUININE SULPHATE.

The quinine sulphate subjected to measurement was prepared by making a saturated solution in water containing a trace of sulphuric acid. The solution was exposed to diffuse daylight in a cubical cell of glass, the faces of which measured 8 cm., and the fluorescence was observed through a slit in one of the faces at right angles to that exposed to the light. This slit was placed as near the corner of the cell as possible, so as to bring the layer of liquid lying next the glass on the exposed side into the field of view. The reference spectrum, as usual, was obtained from the light diffusely reflected from a block of magnesium carbonate, but in this case the surface of the block was illuminated by daylight, so that the fluctuations of intensity might affect both spectra equally and in the same sense.

The transmission of the solution was determined by placing a second block of magnesium carbonate behind the cell and determining the intensity of the light transmitted by the liquid in the various regions as compared with that reflected from the first block. The instrument used in this and in some of the subsequent measurements described in this chapter was a spectroscope whose collimator was furnished with a double Vierordt slit. Light for the comparison spectrum was introduced by means of a right-angled prism and the adjustment of intensities was made in the usual manner by means of micrometer screws.

A second set of measurements with this substance was made with the Lummer-Brodhun spectrophotometer. A mercury-arc lamp was used in place of the Nernst filament of our previous experiments and the ultra-violet line 0.365 μ, isolated by dispersion with the large spectrometer, was employed for excitation. The comparison spectrum in this case was the magnesium block illuminated by means of the acetylene flame.

It is obvious that owing to the different distribution of intensities in the spectra of daylight and of the acetylene flame these two sets of observations would not be strictly comparable. In order, however, to make them at least approximately so, the following correction was applied to the observations by daylight. From certain data obtained by Vogel[1] and published by him many years ago, a curve was plotted giving the distribution of intensities in the spectrum of diffuse daylight with clouded sky, the spectrun of a petroleum-gas flame being taken as the standard. Vogel's measurements agree as well as could be expected, considering the fluctuating character of daylight, with those subsequently made by W. H. Pickering[2] and by Nichols and Franklin.[3] As the sky was overcast at the time of making the observations on quinine sulphate just described, it was assumed that the quality of daylight would on that occasion be represented with sufficient accuracy by means of this curve. By means of a similar curve, giving the distribution of intensities in the spectrum of the acetylene flame as compared with the petroleum flame, it is possible to determine the relation between daylight and the acetylene flame. Vogel's curve for *daylight-petroleum* and the computed curve for *daylight-acetylene* are given[4] in Fig. 13. By means of the latter it is possible, from the observations upon quinine sulphate, to compute a curve in which the light of the acetylene flame reflected from magnesium carbonate is the standard. This curve (*B*, Fig. 14) corresponds precisely, as regards the location of its maximum, with curve *A* in the same figure, which shows the results of the measurement of the fluorescence of this substance when excited by means of the ultra-violet of the mercury lamp. Since these two sets were made with different types of spectrophotometer their agreement affords a desirable check upon the performance of the two instruments.

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[1] Vogel, Berliner Monatsberichte, p. 801, 1880.

[2] W. H. Pickering, Proc. Am. Acad. of Arts and Sciences, vol. 25, 1880.

[3] Nichols and Franklin, American Journal of Science, vol. 38, p. 100, 1889.

[4] The two sources being so adjusted as to have the same intensity at the *D* line, the curve shows the ratio of intensities for other wave-lengths.

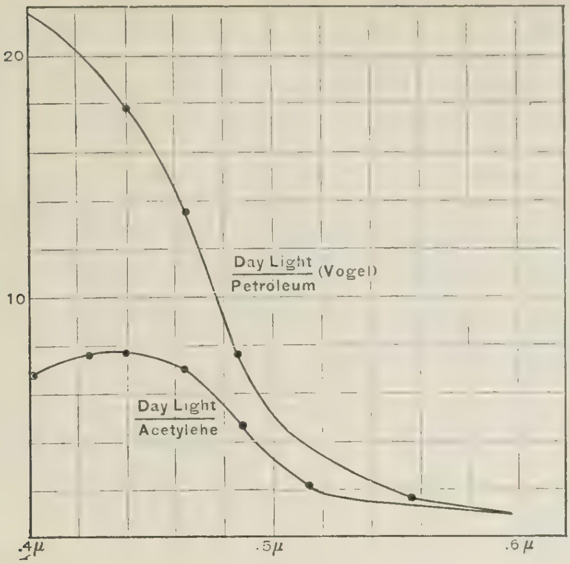

Fig. 13.

Curves for daylight-petroleum and daylight-acetylene.

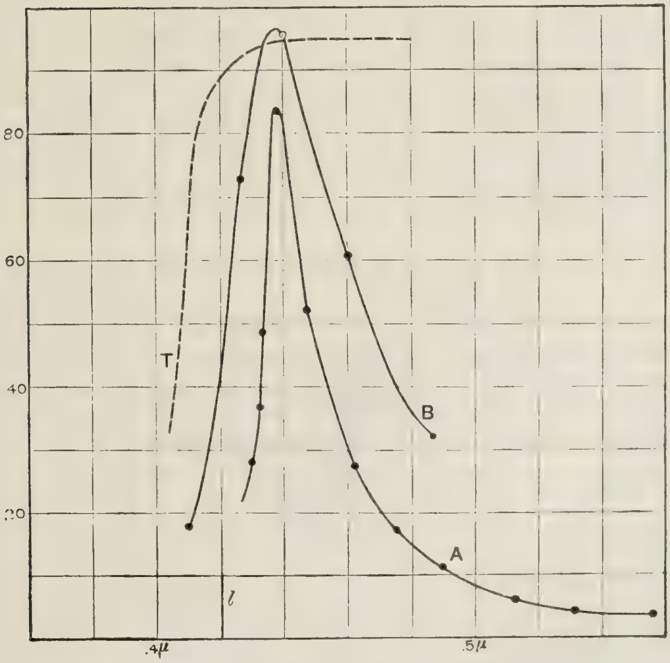

Fig. 14.—Quinine sulphate in water.

Curve *A*. Fluorescence spectrum when excited by Hg line, 0.3650 μ.
Curve *B*. Fluorescence spectrum when excited by daylight.
Curve *T*. Transmission spectrum. Layer 8 cm. thick.

The curve *T* gives the transmission of the solution as measured by the method already described. It was not found possible, owing to the fact that this solution remains transparent almost to the limits of the visible spectrum, to go very far into the absorption band; but the observations suffice to locate the infra edge of the band very closely. To gain further information concerning the nature of the absorption band a series of photographs of the transmission spectrum were taken by means of a Rowland grating with sunlight as the source of illumination. The infra edge of the band, as shown by the disappearance of the Fraunhofer lines, was found to lie in the region indicated by the spectrometric measurements shown in Fig. 14. Absorption became almost complete in the neighborhood of the *H* lines and continued throughout the ultra-violet, at least up to the point where glass becomes opaque.

In order to determine if possible the position of the ultra edge of the band, the quinine solution was placed in a cell with quartz walls and photographs were taken, using an arc light into which zinc had been introduced as a source. Lines due to this metal were distinguishable in the comparison spectrum as far as wave-length 0.2558 μ, to which point the opacity of the solution of quinine sulphate was found to be complete.

It will be seen from the curves *A* and *B* (Fig. 14) that the fluorescence spectrum of quinine sulphate is of the same type as that of the various fluorescent dye-stuffs. It consists of a single band with a sharply defined maximum at 0.437 μ. Since the curves obtained with daylight and with monochromatic light from the mercury arc are identical as regards the position of the maximum and in general form, and since they are of the same type as the various other fluorescence spectra already described, it is evident that quinine sulphate belongs to the same class as fluorescein, eosin, etc. It is true that in the case of this substance it is possible to trace the fluorescent light throughout nearly the entire spectrum, a point which is to be considered further in a subsequent paragraph, but beyond 0.5 μ intensities are very small.

Contrary to the view expressed by Lommel, the fluorescence of quinine sulphate appears to be independent of the wave-length of the exciting light. Since, however, this is one of the substances which has been cited in support of Stokes's law, it was deemed important to determine as carefully as possible the longest wave-length of monochromatic light capable of exciting fluorescence. This is a matter of considerable difficulty on account of the weakness of the effect. By means of the method of double dispersion already described, the electric arc being used as a source, monochromatic light thoroughly free from all stray radiation was obtained. When this was used for excitation the last trace of observable fluorescence was found to disappear at wave-length 0.420 μ.

In no other case have we found this limiting wave-length to lie so close to the ultra edge of the fluorescence band. It will be noted, however, that in making measurements by daylight readings were obtained at wave-length 0.41 μ and the fluorescence under strong excitation is traceable still further into the violet, certainly almost, if not quite, to 0.40 μ. While quinine sulphate then approaches more nearly to conformity with Stokes's law than the other substances that we have studied, the evidence is distinctly in favor of the view that it, like other fluorescent materials, is capable of being excited by all wave-lengths of light lying in or on the infra edge of its absorption band; and that the longest wave-length capable of producing an observable fluorescence is appreciably less refrangible than the shorter wave-lengths of its fluorescence spectrum.

CHLOROPHYLL.

The fluorescence spectrum of chlorophyll was studied by Stokes,[1] who found, in addition to the usual red band, a fainter excitation in the green of the spectrum. Hagenbach[2] subsequently made an exhaustive study of this substance. It was his opinion that it did not conform to the law of Stokes. Lommel[3] placed chlorophyll in his first class, to which belong all substances whose fluorescence is independent of the wave-length of the exciting light.

The solution of chlorophyll used in our measurements was made by digesting green leaves in absolute alcohol and filtering. The transmission curve (Fig. 15) shows four well-defined bands, of which the one to which fluorescence is due is more intense and broader than the others. Measurements made in the extreme red appeared to indicate the presence of still another region of diminished transparency which it was not possible to map with the spectrophotometer. In the hope of determining more definitely the character of this band and of ascertaining whether the series of striking absorption bands in the visible spectrum extends into the infra-red, we requested Mr. W. W. Coblentz, who was engaged in the study of the infra-red by means of a radiometer and a mirror spectrometer with rock-salt

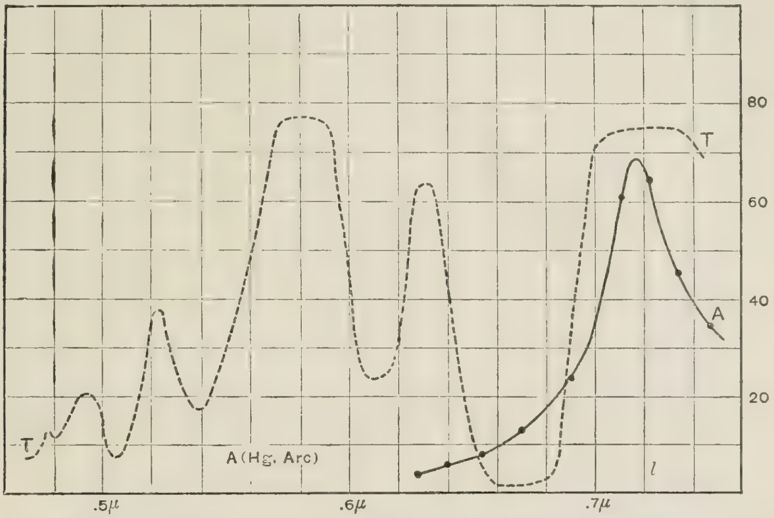

Fig. 15.—Chlorophyll (fresh alcoholic solution from green leaves).

Curve *A*. Fluorescence spectrum when excited by Hg arc.
Curve *T*. Transmission spectrum of a layer 1.1 cm. thick.

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[1] Stokes, Philos. Trans., 1853.
[2] Hagenbach, Poggendorff's Ann., 141, p. 245.
[3] Lommel, *l. c.*

prism, to explore the spectrum of this solution. The results of his measurements are plotted in Fig. 16. His observations extend from 0.61 μ to 1.45 μ, at which wave-length the alcohol in which the chlorophyll was dissolved becomes so nearly opaque as to prevent further readings. The absorption band at 0.675 μ is clearly shown; also the band at the extreme edge of the visible red 0.745 μ. The latter, however, is of little intensity. In Mr. Coblentz's measurements comparison was made between a cell filled with the chlorophyll solution and the same cell when filled with alcohol in which no chlorophyll had been dissolved. The curve therefore indicates the effect of the chlorophyll and other dissolved matters upon the transparency of the alcohol. It will be noted that between 0.8 μ and 0.9 μ the material in solution has no absorbing power. At the latter wave-length absorption again begins to show itself and increases steadily to 1.45 μ, where the transmitting power of the solution is only 60 per cent as great as that of the alcohol itself.

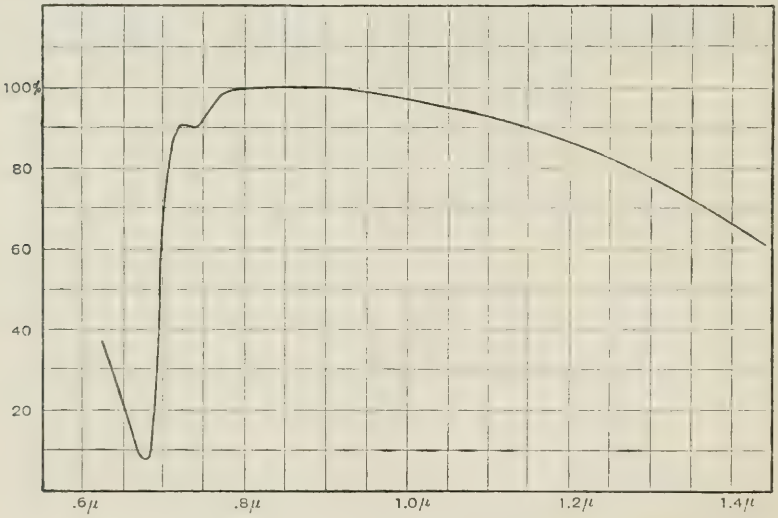

Fig. 16.

Transmission of chlorophyll in the infra-red. (Measurements by W. W. Coblentz.)

In determining the fluorescence curve *A* (Fig. 15), which was obtained by using the green line of the mercury arc (0.546 μ) for excitation, we were able to trace the fluorescence to wave-length 0.624 μ, which lies well beyond the ultra side of the absorption band. This had not been found possible in the case of the fluorescence spectra previously described, partly on account of the greater width of the bands and partly for the following reason. The fluorescence spectrum of chlorophyll is doubtless traceable to an unusual distance toward the violet because the maximum lies in the extreme red, in a region of very low luminosity. Fluorescence in this region, to be appreciable, must be of great intensity, and on the side toward the violet the rapidly falling intensity is largely counterbalanced by increase in luminosity. The same is true of the infra side of the fluorescence band of substances like quinine sulphate; so that, although the curves are of the same type as those described above—fluorescein, etc.— the fluorescence can be followed nearly through the spectrum. The curves of resorcin-blau, fluorite, and æsculin afford other examples of this phenomenon. Where, on the other hand, the maximum is in the middle of the spectrum, as in the case of rhodamin, eosin, fluorescein, etc., the fluorescence soon becomes too small for measurement on both sides of the maximum because of the diminution of luminosity toward the ends of the visible spectrum.

The green fluorescence described by Stokes was faintly discernible under strong illumination, but its intensity would not permit of measurements.

The question of the applicability of Stokes's law to this solution was tested by observing with monochromatic light, by the method already described, the longest wave-length which was capable of producing appreciable fluorescence. The limiting wave-length (0.720 μ), which gave faint but unmistakable fluorescence (see line *l*, Fig. 15), lies on the infra side of the maximum of the curve *A*.

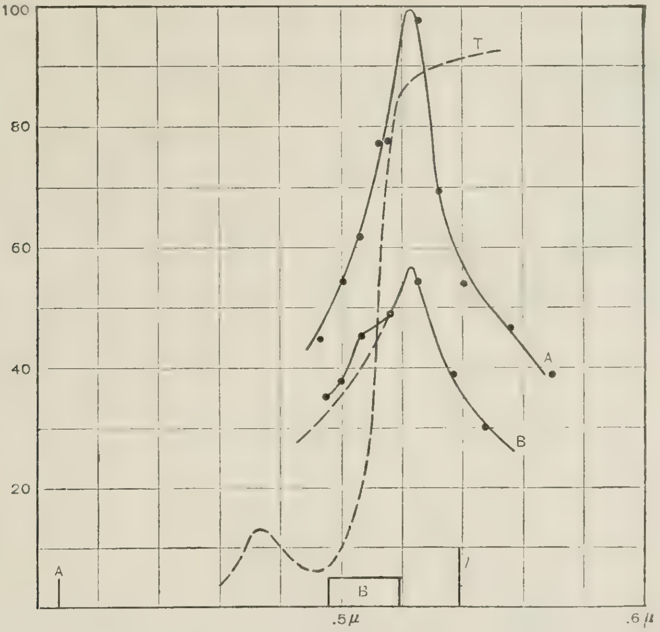

Fig. 17.—Canary glass.

Curve *A*. Fluorescence spectrum when excited by violet light, $\lambda = 0.407\ \mu$.
Curve *B*. Fluorescence spectrum when the exciting light lay in the green, in the region marked *B*.
Curve *T*. Transmission spectrum for a layer 7 cm. thick.

CANARY GLASS.

In our experiments upon canary glass one corner of a rectangular slab 1 cm. in thickness and 7 cm. wide was used. This was mounted in front of the slit of the Lummer-Brodhun spectrophotometer in place of and in a position corresponding to the cell employed in the study of the fluorescent solutions. Fluorescence was excited in the manner already described, by means of light entering the glass at right angles to the axis of the collimator tube. Measurements were made using the Hg line 0.407 μ (see curve *A*, Fig. 17) and green light from the spectrum of the Nernst filament (curve *B*).

To determine the location of the absorption band, light transmitted through the entire width of the glass, giving a layer 7 cm. thick, was measured. The transmission curve *T* shows a minimum but by no means complete opacity at 0.472 μ. The absorption spectrum of this specimen did not exhibit the complex character of that studied and described by Stokes in his memoir already cited. Our quantitative exploration, however, did not extend beyond the determination of the infra edge of the band exciting fluorescence. The fluorescence spectrum, contrary to expectation, appears to belong to the same simple type as that of the fluorescent substances previously examined. The glass was optically very imperfect and the fluorescence measurements were seriously interfered with by the presence of stray light. This shows itself in the case of curve *B*, which is distorted in the regions corresponding in wave-length to the exciting light. The observations upon the ultra side of the curve are, as will be seen from the figure, considerably raised above the probable normal trend of the curve, which is shown by means of the dotted line. Curves *A* and *B*, however, have their maxima at the same wave-length, and, apart from the discrepancy just mentioned, their type corresponds precisely with that of the numerous other fluorescent spectra examined.[1]

In the determination of the maximum wave-length capable of exciting fluorescence it was especially necessary to distinguish between fluorescent light and ordinary diffusion due to the imperfect optical properties of the glass. When one allows light to pass through this glass after being dispersed by a prism the path of the rays remains visible throughout the entire spectrum instead of disappearing for the rays that do not excite fluorescence, as is the case in an optically perfect medium. By means of a Nicol prism held before the eye it was, however, easy to distinguish sharply between fluorescence and ordinary diffusion. The vertical line *l* marks the limiting wave-length (0.539μ) at which fluorescence becomes inappreciable. It lies far to the infra side of the maximum, showing that in this, as in all previous cases, there was not even approximate conformity to the law of Stokes.

It is probable that the glass studied by Stokes, and by means of which he observed such extraordinary fluorescence phenomena, was altogether different from our specimen. It contained perhaps other fluorescent materials in solution which were absent in the glass now under consideration. The glass which we have examined appears to belong in the same class with all the other fluorescent substances upon which measurements were made: its fluorescence spectrum consists of a single band, the location of which is independent of the wave-length of the exciting light, and it does not obey Stokes's law.

FLUORITE.

From a collection of small crystals of fluorspar from Derbyshire, England, placed at our disposal by Professor Gill, of the Department of Mineralogy of Cornell University, two specimens were selected for study. One of these was green by transmitted light, the other colorless. Both showed the well-known blue-violet color due to fluorescence. The transmission

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[1] For an extended study of the fluorescence and absorption of another specimen of uranium glass see R. C. Gibbs, Physical Review, XXVIII, p. 361.

curves of the spectrum of these crystals are brought together for comparison in Fig. 18. Curve *A* of the green spar (thickness 0.8) cm. contains a broad, well-marked band in the yellow and a second rather narrow band to which the fluorescence is due. The maximum of absorption in the latter band is at 0.424 μ. Curve *B*, which relates to the white crystal, contains only the second band. This crystal, although thicker (1.72 cm.), is more transparent, the absorption in the middle of the band being less than 50 per cent. It is interesting to note the presence of easily measurable fluorescence accompanying such feeble absorption.

The fluorescence of the green crystal was determined by means of the undispersed light of the carbon arc (curve *A*, Fig. 19) and of the mercury arc direct (curve *B*). The effective light from the latter source comes chiefly from the lines 0.407 μ and 0.365 μ. The fluorescence conforms strictly to that of all substances previously examined by us. The spectrum consists of a single band, the maximum of which at 0.433 μ is independent of the character of the exciting light.

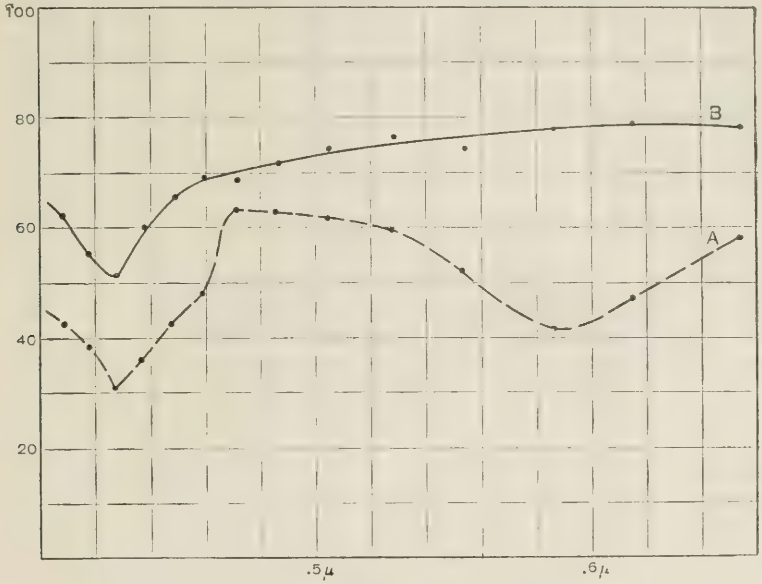

Fig. 18.

Transmission spectra of green fluorspar (*A*) and white fluorspar (*B*).

In the measurement of the fluorescence of the white crystal diffuse daylight was employed, and the observations were made with the spectroscope with a single collimator tube and Vierordt slit, already described. The two sets of readings obtained are plotted in Fig. 20. The curves correspond very closely in character with those obtained with the green fluorite, although the maximum appears to be shifted very slightly toward the violet. This shift may be due to a combination of errors of observation and of instrumental errors, the instruments employed being different throughout, or it may result from some slight difference in the character of the absorption band. It will be noticed by reference to Fig. 18 that the infra edge of the absorption band of the green crystal does not rise so

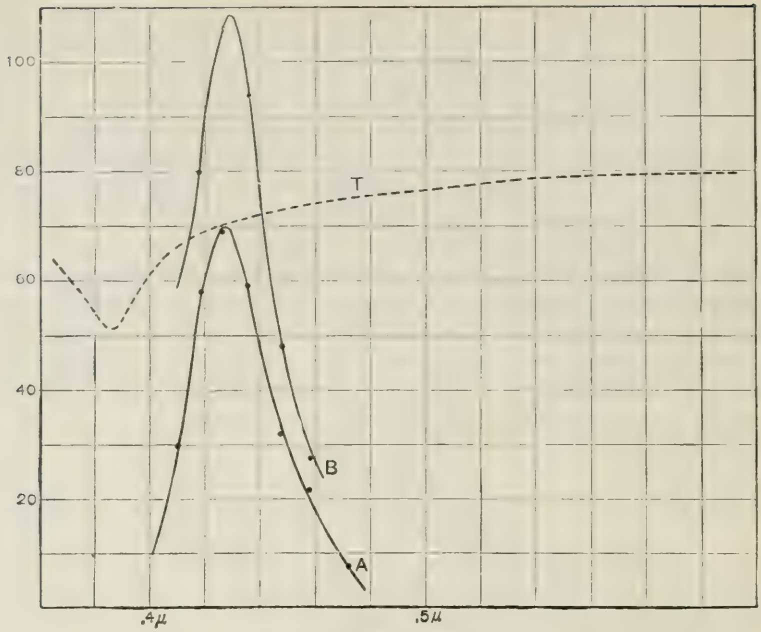

Fig. 19.—White fluorite.

Curve *A*. Fluorescence spectrum when excited by the carbon arc.
Curve *B*. Fluorescence spectrum when excited by Hg arc.
Curve *T*. Transmission spectrum of a layer 0.8 cm. thick.

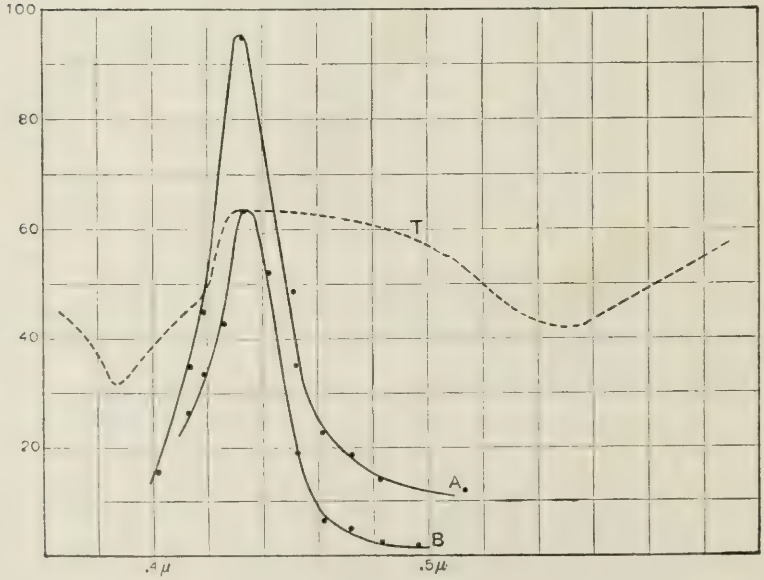

Fig. 20.—Green fluorite.

Curve *A*. Fluorescence spectrum when excited by diffuse daylight.
Curve *B*. The same repeated on another day.
Curve *T*. Transmission spectrum of a layer 1.72 cm. thick.

sharply as is the case of the white fluorite. The broadening of the band upon this side may result in a slight shifting of the fluorescence. It has already been shown by Stenger[1] and by O. Knoblauch[2] that fluorescent substances such as eosin and naphthalin-roth have the position of the fluorescent spectrum shifted by dissolving them in different liquids; and that the shift corresponds with that of the absorption band previously described by Kundt.[3]

ÆSCULIN.

This substance was cited by Lommel[4] as typical of his second class, the characteristics of which are a fluorescence spectrum independent of the wave-length of the exciting source and an absorption band beginning at that point in the spectrum at which the first trace of fluorescence shows itself and extending toward the violet, so that there is no overlapping of the band of the exciting light with the fluorescence spectrum.

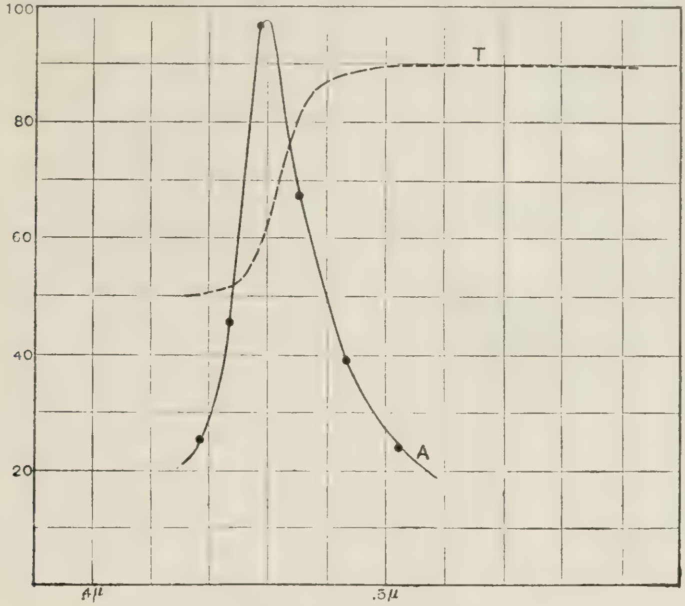

Fig. 21.—Æsculin (from horse chestnut).

Curve *A*. Fluorescence spectrum when excited by arc light.
Curve *T*. Transmission spectrum of a layer 8 cm. thick.

Our measurements of the fluorescence of æsculin were made upon a solution consisting of water in which freshly broken twigs of the horse-chestnut tree had been immersed. When freshly prepared this shows the well-known fluorescence characteristic of æsculin, but the solution loses its activity upon standing. We were unable to procure pure æsculin, but the results, so far as the form and composition of the fluorescence curve are concerned, would probably be the same had measurements been made upon the solution of the chemically prepared substance. The fluorescence curve, Fig. 21, is of the usual form and its position with reference to the

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[1] Stenger, Wied. Ann., 28, p. 201.

[2] O. Knoblauch, Wied. Ann., 54, p. 193.

[3] Kundt, Wied. Ann., 4, p. 34, 1878.

[4] Lommel, Poggendorff's Ann., 143, p. 38.

transmission curve T is similar to that of the substances previously examined. On the infra side, as has been pointed out by Lommel, it is possible to trace the fluorescence throughout the entire spectrum; but this, as in the instances already considered, is due to the greater luminosity as we move toward the middle of the spectrum rather than to any unusual maintenance of the intensity of the fluorescence in that direction. The band falls off quite sharply on that side, differing not at all in this respect from the bands of other substances, such as quinine sulphate and fluorite. The measurement of the transmission showed a very dilute solution, in which the maximum of absorption is scarcely more marked than in the case of the bands of the specimens of fluorite already described.

From the location of the absorption band with reference to the maximum of fluorescence it would be safe to predict for this substance, on the basis of previous experience, a wide divergence from the law of Stokes. Determination of the limiting value of the exciting light is somewhat difficult to make. It was found, using the spectrum of the arc lamp as a source, that the fluorescence due to light of wave-length 0.45 μ could still be discerned.

It is not possible, with the spectrophotometer, to make a complete exploration of the absorption band of æsculin, since the band extends into the ultra-violet. Photographs of the absorption spectrum of this solution, made by Miss Eleanor Burns at our suggestion, show this band to be comparatively narrow, its ultra edge lying at about 0.34 μ, beyond which there is no absorption capable of detection by photographic means.

There is nothing in these measurements which would lead one to place æsculin in a class different from that of the foregoing substances. It is distinguished, as regards the character of its fluorescence spectrum, from quinine sulphate and fluorite, the other two substances on our list the fluorescence of which lies in the blue, only in that the maximum lies at a somewhat greater wave-length. The curve A, Fig. 21, was obtained by the use of the direct light of the arc, undispersed. Since the curve corresponded in every form to the general type it did not seem necessary to repeat the observations with exciting light of other composition.

SUMMARY.

From the measurements described in this chapter the following conclusions may be drawn:

1. Eosin, naphthalin-roth, fluorescein, rhodamin, resorcin-blau, quinine sulphate, chlorophyll, canary glass, green fluorspar, white fluorspar, and æsculin all exhibit fluorescence of the same type.
2. The fluorescence spectrum in general consists of a single band situated near the infra edge of the absorption band with which fluorescence is associated.
3. The position of the maximum of the fluorescence band is in all cases independent of the wave-length or composition of the exciting light.
4. The distribution of intensities in the fluorescence spectrum is independent of the wave-length of the exciting light.
5. Stokes's law holds for none of the numerous fluorescent substances thus far examined.

CHAPTER II.

ON THE ABSORBING POWER AND THE FLUORESCENCE OF RESORUFIN.

The experiments described in this chapter were undertaken at the suggestion of the authors by Miss Frances G. Wick. An account of them was first given in the Physical Review.[1] The chief object was to determine whether the typical fluorescence spectrum changes with the concentration of the solution or whether the shift of the band referred to in Chapter I is caused by absorption only. The substance studied was resorufin, whose strong fluorescence in the yellow-red is conveniently excited and readily observed.

It has frequently been observed that the color of the light emitted by a fluorescent solution is altered by a change in the concentration of the solution. A dilute solution of fluorescein, as indicated in Chapter I, gives a green fluorescence, while the light emitted by a concentrated solution of the same substance shows a distinctly yellow tinge. In other words, an increase in concentration causes the maximum of the fluorescence spectrum to shift toward the longer wave-lengths.

Such a shift might result from a real change in the period of vibration of the fluorescent molecules, *i. e.*, the form of the typical fluorescence spectrum might depend upon the concentration of the solution. But the observed change in the fluorescence spectrum might equally well result from a change in the absorbing power of the solution. The light emitted by portions of the active substance in the interior of the solution must pass through the solution before emerging, and is therefore weakened by absorption. Since the maximum of the fluorescence spectrum does not occur at the same wave-length as the maximum absorption, being always slightly displaced in the direction of the longer waves, it is clear that different portions of the fluorescence spectrum will be affected by absorption in varying degree; the shorter waves will always be absorbed most strongly. The maximum of the fluorescence spectrum is therefore always shifted toward the red to some extent, and the increased absorbing power of concentrated solutions causes the shift due to this cause to increase with the concentration.

The experimental work naturally falls under three heads, as follows:

1. The relation between absorption and thickness, to test whether or not the absorption of a fluorescent solution obeys the exponential law of optically perfect substances.

2. The relation between absorption and concentration, to test the application of Beer's[2] law, *i. e.*, that an increase in the concentration of a solution is equivalent to an increase in thickness.

3. The study of fluorescence spectra of solutions of resorufin of different concentrations to determine whether or not there is any shift in the maximum of fluorescence as concentration changes.

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[1] Frances G. Wick, Physical Review, XXIV, p. 356.

[2] Beer, Poggendorff's Ann., 86, p. 78.

HISTORICAL.

In 1888 B. Walter,[1] using the Vierordt spectrophotometer, found the ratio of the fluorescent light emitted to total incident light absorbed, Fl/A, to increase with dilution. This law had been previously conjectured by Lommel,[2] whose mathematical theory Walter[3] used in verifying his own results. In connection with this work Walter tested Beer's law of absorption for fluorescein by four measurements. He found the law to hold true for dilute but not for concentrated solutions.

Walter briefly states his conclusions as follows:

> "Ability to excite fluorescence, Fl/A, in the most concentrated solutions, is infinitely small or zero. After Fl/A obtains a measurable value it increases in proportion to dilution to a certain dilution called the 'critical point.' For greater dilutions Fl/A remains constant."

In explanation of the above, Walter[4] advances a molecular-group theory which is of interest, preceding as it does the present theory of ionization given by Buckingham.[5] Walter summarizes his theory in the following statements:

1. Every separate molecule of a given substance in solution absorbs, so long as it remains in the separate condition, the same fraction of the light falling upon it, no matter how great its distance from other molecules in the solution may be.

2. Every separate molecule of a given fluorescent substance in solution, so long as it is in the separate condition, changes the same fraction of absorbed light into fluorescent light, no matter how great its distance from neighboring molecules may be.

3. As soon as molecules begin to combine in groups the validity of these statements ceases. Fluorescence entirely ceases in such a group and absorption extends over wave-lengths which a separate molecule is not able to absorb.

Walter's idea of the separate molecule seems to correspond closely with what is now known as the ion.

In 1894 E. Buckingham[6] performed a series of careful experiments to discover whether or not fluorescent substances are in a state of ionization. His investigations led to the conclusion that, at least in some cases, fluorescence is due to ionization and produced only by that part of a solution which is ionized. Certain ions, along with their other well-known optical properties, possess this property of fluorescence.

The conclusions drawn from the spectrophotometric work described in Chapter I are found to apply also to resorufin. For example:

1. The characteristic fluorescence band is situated near the edge of the absorption band and is steeper on the side toward the violet.

2. As fluorescent light passes through greater thicknesses of liquid, the position of the maximum in the fluorescence spectrum is shifted toward the red.

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[1] B. Walter, Wied. Ann., 34, 1888.

[2] Lommel, Poggendorff's Ann., 160, p. 76, 1877.

[3] B. Walter, Wied. Ann., 36, p. 502, 1889.

[4] B. Walter, Wied. Ann., 36, p. 518, 1889.

[5] E. Buckingham, Zeitschrift für physikalische Chemie, 14, p. 129, 1894.

[6] E. Buckingham, *l. c.*

3. The effect of diluting a fluorescent solution is similar to that of diminishing the distance through which the fluorescent light travels.

METHOD OF OBSERVATION.

The instrument used for this work was the spectrophotometer of Lummer and Brodhun.

The source of light was an acetylene flame *S* (Fig. 22) from which light was diffusely reflected by a block of magnesium carbonate, *n*, mounted at an angle at 45° with axis of the collimator *A*. For observations on transmission a similar block of magnesium carbonate was placed in front of the slit *D*.

The work was performed in a room with black walls, the acetylene flame being the only source of light. Screens were adjusted so that no stray light could strike any part of the instrument.

The solution under consideration was placed in front of slit *D*, the width of which was kept constant during a single set of observations. The ocular lenses of the telescope were removed, the eye being focused upon the face of the prism magnified by the objective of the telescope *T*.

In making observations the width of slit *C* was adjusted by means of a micrometer screw until the central band of light reflected from *KL* was brought into the best possible coincidence with that transmitted from *D* through the upper and lower parts of the cube. The results given represent an average of from 5 to 10 settings, the zero point of the screw attached to *C* being carefully determined and care being taken to avoid errors due to lost motion.

The hydrogen lines of a vacuum tube, together with a few of the Fraunhofer lines, were used for calibration.

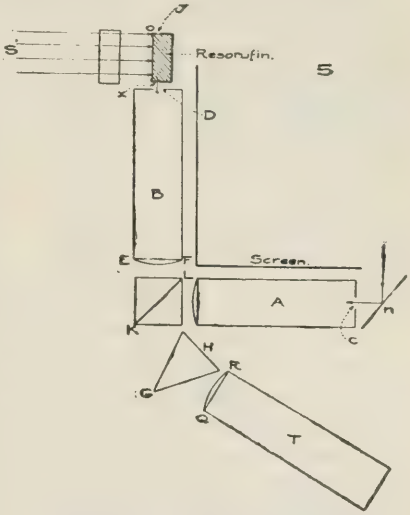
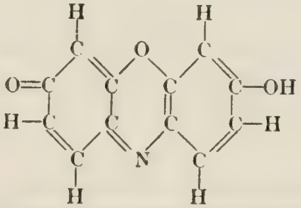


Fig. 22.—Apparatus arranged for measuring fluorescence.

COMPOSITION OF RESORUFIN.

Weselski's diazo-resorufin,[1] the fluorescent substance used in this investigation,[2] has the formula



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[1] Berichte der deutschen chemischen Gesellschaft, 22, 3036.

[2] Acknowledgment should be made to Prof. W. R. Orndorff for his kindness in preparing the resorufin used in this work.

Dissolved in absolute alcohol it is bright red in color, with a sharply defined fluorescence band extending from 0.54μ to the limits of the visible spectrum in the red. The transmission spectrum given in Table 2 and Fig. 23 shows the absorption band corresponding to this, and also a smaller absorption band in the violet.

Different concentrations of resorufin were used. These are merely relative and are indicated as "concentration $\frac{1}{2}$, $\frac{1}{4}$, $\frac{1}{8}$, $\frac{1}{16}$, $\frac{1}{32}$, $\frac{1}{64}$, and $\frac{1}{128}$," the original solution being taken as $\frac{1}{1}$. All curves corresponding to the above concentrations are indicated by the letters *A*, *B*, *C*, *D*, *E*, *F*, and *G* respectively.

TABLE 2.

Transmission through layer of resorufin 1.075 cm. thick. Concentration $\frac{1}{8}$. λ = Wave-length. I_0 = Intensity of light before transmission. I = Intensity of light after transmission.

λ	I_0	I	$\frac{I}{I_0}$ = Transmission.	λ	I_0	I	$\frac{I}{I_0}$ = Transmission.
0.384μ	45	6	0.111	0.48μ	45.72	32.05	0.70
.39	46	12	.261	.492	45.72	28.87	.63
.394	46	20.25	.438	.508	44.7	24.4	.538
.407	46	16	.347	.524	44.7	17.57	.394
.413	46	13.62	.297	.542	46.27	11	.241
.42	46	9.75	.213	.562	46.41	7.52	.162
.429	46	9.95	.217	.589	46.25	11.64	.253
.438	45.5	12.1	.266	.614	46.55	32.27	.706
.448	45.5	14.15	.32	.646	46.62	45.62	.981
.457	45.05	22.27	.497	.69	44.52	44	.99
.468	45.05	25.97	.579	.72	41.25	41	.99

ABSORPTION AND THICKNESS.

The first problem under consideration was, as stated above, to find whether a fluorescent solution acts like an optically perfect substance in obeying Lambert's law of absorption, *i. e.*, whether

$$I = I_0 e^{-\beta x}$$

where I_0 and I are the intensities before and after transmission, and x is the thickness of the absorbing layer.

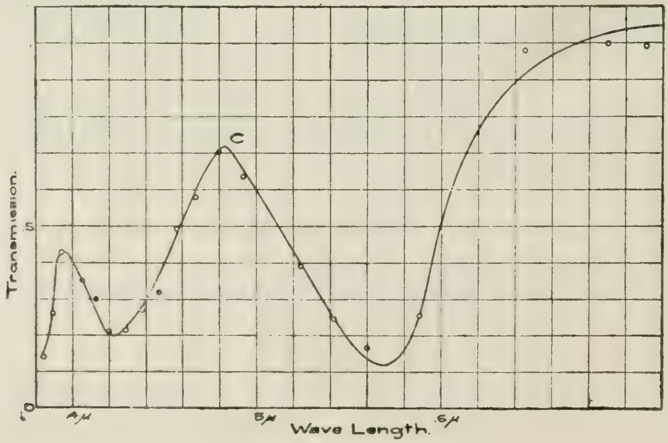

Fig. 23.

Transmission spectrum of layer 1.075 cm. thick. Concentration $\frac{1}{8}$.

To test this law the coefficient of absorption, β, was calculated from observations taken with cells of different inside thickness, the measurements of these cells being made with great care.

The larger cell was measured with micrometer calipers. Thickness of glass $=\alpha$, β (Fig. 24). Outside thickness of that part of the cell used for transmission $=C$. Inside thickness $=T$.

$$T=C-(\alpha+\beta)=2.05 \text{ cm.}$$

In the case of small cell (Fig. 25), calipers could not be used to measure the thickness of glass. The cell was placed under a traveling microscope to measure the average inside thickness of the top. The outside thickness at the points indicated in the figure was measured with calipers.

$$T=T'+(n-m)=1.075 \text{ cm.}$$

It was assumed that the thickness of glass from top to bottom of cell remained constant, since broken pieces of the same glass varied not more than 0.01 mm.

To determine the transmission, the cell containing the resorufin was placed in front of slit D (Fig. 22), care being taken that no direct light from S should strike the cell, and light from the block of magnesium carbonate, in front of slit D (not shown in the figure), was transmitted through it. The reading of C was taken to get the relative intensity, I, of the light transmitted for different wave-lengths. After each observation the cell containing resorufin was removed and an identical one filled with absolute alcohol put in its place. The reading of C in this case gave the intensity of the incident light before absorption, I_0. From these observed values of I_0 and I, together with the thickness of the absorbing layer, the coefficient of absorption was computed. If the loss by reflection may be regarded as the same for the cell containing resorufin as for that filled with alcohol—and the difference must be extremely small—it will be seen that the influence of reflection is to introduce a factor, $1-R$, in the case of both settings, and that this factor will disappear when the ratio is taken.

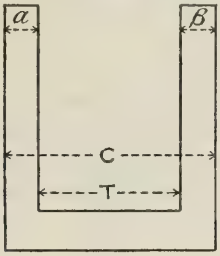

Fig. 24.

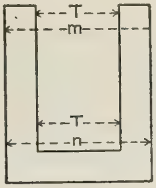

Fig. 25.

As a check upon these results a different method of observation was used. Keeping D (Fig. 22) constant, the reading C_1 was taken for the light alone. A reading of C_2 was then taken with alcohol in front of C and resorufin in front of D.

$$\frac{C_1}{D}=\text{Incident light }(I_0) \qquad \frac{C_2}{D}=\text{Transmitted light }(I) \qquad \frac{\frac{C_1}{D}}{\frac{C_2}{D}}=\frac{C_1}{C_2}=\frac{I}{I_0}$$

As a further check the positions of alcohol and resorufin were reversed, the alcohol being placed in front of D and the resorufin in front of C. Then

$$\frac{D}{C_1}=I \qquad \frac{D}{C_2}=I_0 \qquad \frac{I}{I_0}=\frac{C_2}{C_1}$$

It will be noticed that in this method also the disturbances due to reflection from the surfaces of the cells are eliminated.

From these data the value of the coefficient of absorption for each wavelength was found to be practically the same as that found by the first method and independent of the thickness of the cell. Absorption curves plotted from average values obtained by both methods, using cells of two thicknesses, are identical, as shown in Fig. 26.[1] The absorption coefficients for different concentrations and also the data from which the computation was made are given in Table 3.

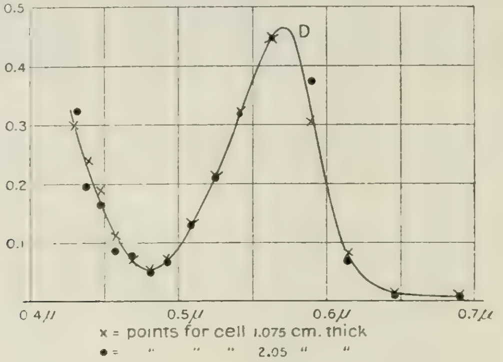

Fig. 26.

Coefficient of absorption as computed from cells of different thickness.

TABLE 3.

Coefficient of absorption computed from cells of different thickness. Concentration $=1/16$. I_0=Intensity of light before transmission. I=Intensity of light after transmission. β=Coefficient of absorption.

λ	Thickness of cell=1.075 cm.			Thickness of cell=2.05 cm.		
	I_0	I	β	I_0	I	β
0.429μ	79.9	35.8	0.7476	81.8	19.9	0.6884
.438	78.8	48.4	.4539	80.0	25.9	.5495
.448	80.2	53.6	.3746	82.4	33.7	.4363
.457	79.5	62.5	.2223	80.6	48.3	.2495
.468	81.6	66.1	.1805[2]	80.4	54.5	.1702[2]
.48	78.9	70.0	.1175[2]	82.3	61.3	.1267[2]
.492	76.1	64.8	.15	80.5	57.0	.1678
.508	76.5	57.5	.2653	79.7	43.1	.2993
.524	76.8	45.8	.4808	78.9	29.5	.4786
.542	75.6	34.5	.7283	78.5	17.3	.7369
.562	75.9	25.4	1.02[2]	78.7	10.0	1.0304[2]
.589	75.8	30.9	0.8354	79.4	18.9	0.6979
.614	75.1	63.4	.1579	79.8	54.0	.1899
.646	73.6	72.2	.0169	80.9	75.8	.0316
.69	64.9	63.8	.0148	71.3	69.2	.0144

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[1] Figures 26, 27, and 28 give only relative values of coefficients, since they are drawn from data computed upon the basis of ordinary instead of natural logarithms. To get from the curves the absolute value of the coefficients given in the tables multiply by 2.3.

[2] These values are average results from a number of observations.

It appears, therefore, that the absorption of resorufin is in accordance with Lambert's law. Deviations from this law, if present, are at least too small to be detected by the experimental methods used.

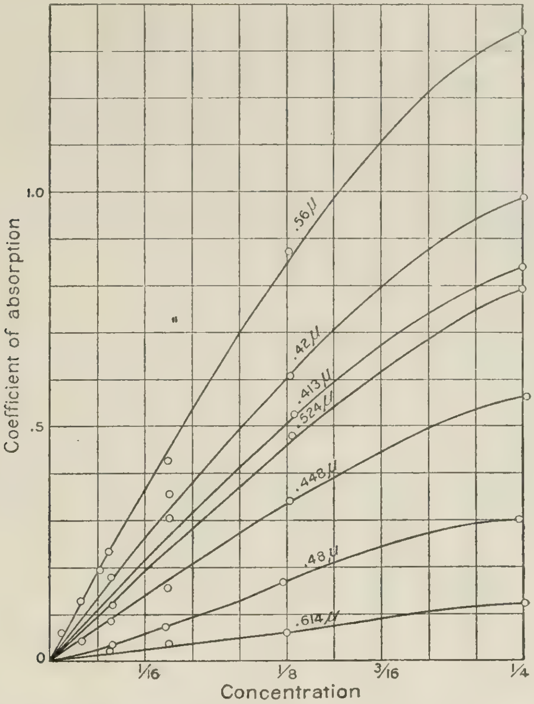

Fig. 27.

Curves showing effect of change in concentration upon coefficient of absorption[1] of wave-lengths marked on curves.

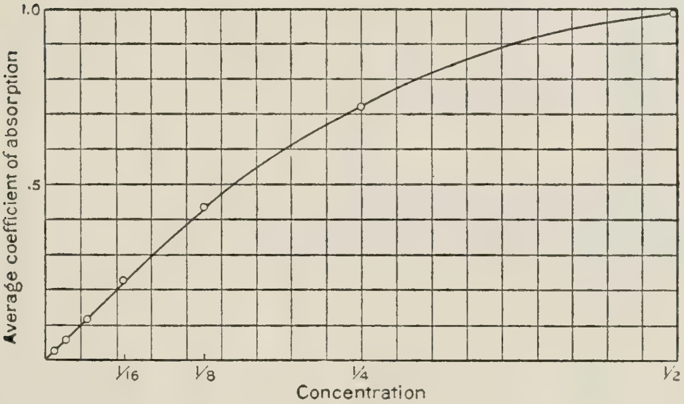

Fig. 28.

Average coefficients of absorption[1] for different concentrations taken from Table 4.

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[1] See footnote on page 30.

ABSORPTION AND CONCENTRATION.

The second set of experiments was undertaken to study the relation between absorption and concentration and thus test the validity of Beer's law for a fluorescent substance, *i.e.*, "increasing the concentration of a solution is equivalent to a like increase in thickness."

The same method of observation was employed for this as for the preceding work, no changes in the apparatus being necessary. The coefficient of absorption was found for different concentrations, the solution being placed in a cell 2.05 cm. thick if dilute, and in cell 1.075 cm. thick if concentrated. This change of cell is permissible, since, according to the results obtained above, Lambert's law of absorption applies to resorufin. The absorption coefficient for different wave-lengths was thus obtained for seven concentrations.

TABLE 4.

Coefficient of absorption for corresponding wave-lengths in different concentrations.

λ	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{8}$	$\frac{1}{16}$	$\frac{1}{32}$	$\frac{1}{64}$	$\frac{1}{128}$
0.413μ	2.254	1.8814	1.2132	0.7125	0.3107	0.1444	0.0276
.42	2.806	2.2793	1.4237	.8533	.4360	.1984	.0775
.448	2.53	1.5364	0.7935	.3565	.1860	.0897	.0368
.48	1.336	0.6934	0.3864	.1734	.0749	.0586	.0367
.524	3.162	1.8584	1.1247	.5349	.2783	.1453	.0692
.562	3.473	3.0797	2.0171	.989	.5441	.3036	.1442
.614	0.3864	0.3082	0.1550	.0995	.0484	.0524	.0265
Average	2.2782	1.6624	1.0162+	0.5313	0.2683	0.1417	0.0597

Figs. 27 and 28 give the results of these observations. It will be noticed from these curves that the coefficient of absorption, in the case of dilute solutions, increases in direct proportion to concentration. For concentrated solutions this proportion fails, the concentration increasing more rapidly than the absorption. This is true for all the wave-lengths; in every case the curve starts out as a straight line for dilute solutions and bends downward as higher concentrations are reached.

TABLE 5.

Coefficients of absorption computed from average of careful observations for concentration $\frac{1}{16}$ and average absorption concentration curve. (Fig. 28).

	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{8}$	$\frac{1}{16}$	$\frac{1}{32}$	$\frac{1}{64}$	$\frac{1}{128}$
0.524μ	2.1986	1.60471	0.9841	0.51313	0.2599	0.12995	0.0651
.542	3.266	2.385	1.455	0.76245	.38398	.19251	.09637
.562	4.3608	3.175	1.946	1.0177	.5154	.25783	.1288
.589	2.7324	1.995	1.219	0.63733	.3227	.16146	.0807
.614	0.49335	0.36087	0.22157	0.115322	.05842	.0292	.0146
.646	0.95588	0.0698	0.0428	0.0223	.0113	.00575	.00283

Fig. 28 shows the average coefficient of absorption for the seven wave-lengths as a function of the concentration. This curve is used later for finding the coefficient of absorption for different dilutions, especially careful measurements for the concentration $\frac{1}{16}$ being taken as a basis of calculation. The values thus obtained, given in Table 5, were used in all subsequent computations involving the coefficient of absorption.

The above results agree, in every respect, with those given by Walter.[1] Beer's law is true for dilute solutions, but fails for greater concentrations, as is indicated by the deviation of the curve from a straight line. The straight form of the curve (Fig. 28) up to concentration $\frac{1}{8}$ corresponds to what Walter calls "complete solution," in which he says the molecules are in a "separate state." Concentration $\frac{1}{8}$ may be regarded as his "critical dilution," where a change seems to take place in the condition of the fluorescent substance. Solutions more concentrated than $\frac{1}{8}$ correspond to those called by Walter "incomplete," in which "molecular groups" exist.

Interpreted according to the ionization theory, the curve (Fig. 28) indicates that in dilutions less than $\frac{1}{8}$ a state of complete or nearly complete ionization has been reached. At this point a change takes place, more resorufin being contained in the solution than is ionized. As the concentration increases, more and more of the solution remains undissociated. It appears that the undissociated resorufin is not only incapable of fluorescence, but is also much less effective in causing absorption than is the dissociated substance.

FLUORESCENCE AND CONCENTRATION.

For observation of the fluorescence spectrum the spectrophotometer was adjusted as before. In front of slit D (Fig. 22) was placed a glass cell 5.4 cm. long, containing the resorufin solution. This cell was entirely covered with black paper, except for a space about 1.5 cm. high across the bottom of the face next to the exciting light S', and two narrow strips, x and y, The opening x was to allow light to enter the collimator slit, while y, directly opposite, was used only for adjusting. The source of illumination used to produce fluorescence was a bank of four acetylene flames S′. Between these and the fluorescent solution was placed a glass cell filled with water to prevent the heating of the resorufin. The comparison source was another acetylene burner S, light from which was reflected into the slit C by a block of magnesium carbonate n. The cell containing the resorufin was so placed that light from the whole layer of solution next the inside surface of glass came through the slit D of the collimator.

It is clear that a portion of the fluorescent light is absorbed by the solution before reaching D, and attention has already been called to the fact that this absorption will be different for different parts of the fluorescence spectrum. If the fluorescence is measured in the manner indicated above it is therefore necessary to apply a correction for absorption before the typical fluorescence spectrum can be determined. Two methods of making this correction have been used. In the first method the necessary correction was computed as follows:

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[1] B. Walter, Wied. Ann., 36, pp. 502 and 518, 1889.

Let *P* be any point in the slit (Fig. 29). The source of the light reaching *P* is a cone in the fluorescent liquid converging toward *P*. The angle of this cone is determined by the aperture of the object glass, *EF*, of the collimator. Any part of this cone cut off by the glass walls of the cell or by the upper surface of the solution is supplied by total reflection.

Consider a disk bounded by two circular sections of this cone at distances x and $x+dx$ respectively from the apex *P* (Fig. 30). The amount of fluorescent light reaching *P* from such a disk as this will be independent of x, provided no absorption takes place, for, while the area of the section varies as x^2, the intensity of the light reaching *P* from each small portion of the disk varies as $1/x^2$. The fluorescent light that would reach *P* from such a disk if there were no absorption is therefore kdx, where k is a function of the wave-length, λ.

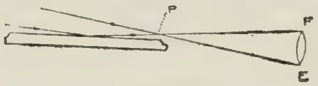

Fig. 29.

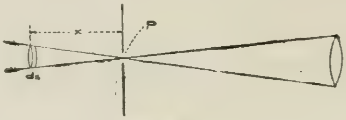

Fig. 30.

Since the light emitted by each section of the cone is in part absorbed, we have for the light reaching *P* from one of the disks

$$di = kdx \,.\, e^{-\beta x}$$

and the total light reaching *P* from the whole cone is

$$i = k \int_0^a e^{-\beta x} dx$$

where a is the thickness of the fluorescent solution. Hence

$$i = k \,.\, \frac{1-e^{-\beta}}{\beta} \text{ and } k = \frac{\beta i}{1-e^{-\beta a}}$$

While the i in this expression represents the light reaching one infinitesimal portion of the slit, it is clear that the total light reaching the slit is proportional to i. It is also evident that k is proportional to the total amount of light, f, of the wave-length considered, that is emitted by the fluorescent substance per unit volume. Hence

$$f = \frac{k\beta I}{1-e^{-\beta a}}$$

The curve showing the relation between f and λ is the "typical fluorescence spectrum."

To investigate the effect of concentration upon the position of the fluorescence band observations were made in six concentrations. Table 6 gives values of observed fluorescence before any correction is made for absorption. Table 8, graphically represented in Fig. 31, gives the same sets of observations so reduced in scale as to be comparable in intensity with each other. This reduction was made by multiplying the data for each concentration by such a factor as to give wave-length 0.589 μ the same value as that of the observed fluorescence of the corresponding concentration in Table 9.

TABLE 6.

Observed fluorescence intensity before correction is made for absorption. Measurements made according to Method I; fluorescence excitation extending over whole face of cell.

λ	$\frac{1}{4}$	$\frac{1}{8}$	$\frac{1}{16}$	$\frac{1}{32}$	$\frac{1}{64}$	$\frac{1}{128}$
0.524μ	1.77	2	2.1	2	2.08	2.4
.542	1.86	2.1	2.2	2	2.13	2.41
.562	3.46	4.67	5.61	7.66	7.43	7.27
.589	30.3	46.4	56.6	34.9	23.2	16.2
.614	79.5	95.5	95.3	34.0	17.63	11.6
.646	86.6	76.3	66.3	17.7	8.9	6.88
.69	59.3	42.4	46.2	12.7	7.28	

TABLE 7.

Observed fluorescence intensity reduced to such a scale as to make intensity of wave-length 0.589 μ the same as observed fluorescence in Table 9.

λ	$\frac{1}{4}$	$\frac{1}{8}$	$\frac{1}{16}$	$\frac{1}{32}$	$\frac{1}{64}$	$\frac{1}{128}$
0.524μ	5.38	4.08	3.19	3.32	3.58	3.12
.542	5.65	4.28	3.34	3.32	3.66	3.23
.562	10.5	9.53	8.53	12.7	12.8	9.73
.589	92.2	94.6	86.1	57.9	40.4	21.8
.614	241.6	195	145	56.5	30.3	15.6
.646	263	155	101	29.4	15.3	9.22
.69	180	86.5	70.3	21.0	12.5	

TABLE 8.

Corrected fluorescence. Value of f calculated from Table 6 according to formula $f = I\beta/(1-e^{-\beta a})$.

λ	$\frac{1}{4}$	$\frac{1}{8}$	$\frac{1}{16}$	$\frac{1}{32}$	$\frac{1}{64}$	$\frac{1}{128}$
0.524μ	2.84	1.97	1.15	0.67	0.53	0.52
.542	4.44	3.06	1.74	0.86	0.632	0.566
.562	11.0	9.09	5.73	4.20	2.56	1.85
.589	60.4	56.6	37.2	13.62	6.35	3.66
.614	33.3	29.8	23.5	7.27	3.45	2.20
.646	19.3	15.5	12.8	3.34	1.65	1.22

TABLE 9.

Intensity of fluorescence of different concentrations at wave-length 0.589 μ.

	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{8}$	$\frac{1}{16}$	$\frac{1}{32}$	$\frac{1}{64}$	$\frac{1}{128}$
Observed fluorescence.	75.5	92.17	94.64	86.06	57.95	40.01	21.68
Corrected fluorescence, *i. e.*, value of *k* as obtained from formula.	206	184	115	54.8	22.5	11.0	4.86

The curves in Fig. 31 show the observed values of I as a function of λ for six different concentrations of the solution. The shift in the maximum caused by a change in concentration is here well marked.

Table 8 gives the result of correcting values in Table 6 for absorption according to the above formula, the value of f, which is proportional to actual fluorescence intensity (see page 34), being found in each case. These values are plotted in Fig. 32 according to an arbitrary vertical scale which makes the height of each curve approximately proportional to intensity of fluorescence for the corresponding concentration. It will be observed that these curves are similar in form, the maximum wave-length being approximately the same, about 0.595 μ.

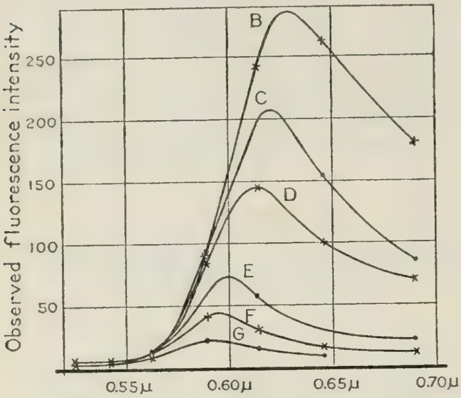

Fig. 31.

Observed fluorescence intensity, showing shift of maximum, with change in concentration.

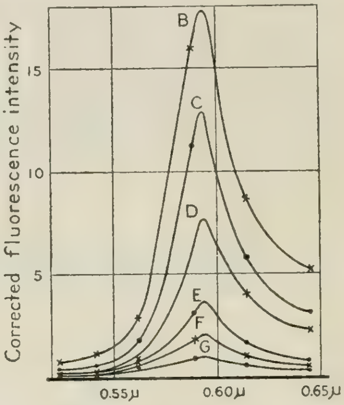

Fig. 32.

Fluorescence curves corrected for absorption.

For purposes of comparison a series of measurements was made to determine the relative intensity of different concentrations at wave-length 0.589 μ, keeping all conditions constant. Table 9 shows the results. In Fig. 33 the curve marked O gives the actual observed fluorescence. The

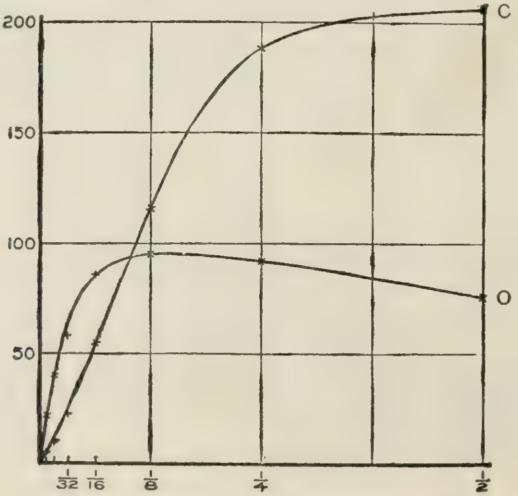

Fig. 33.—Concentration and fluorescence.

Intensity of observed and corrected fluorescence for different concentrations at wave length 0.589 μ.

"corrected" curve, *C*, has for ordinates the value of *f* computed from the formula (page 34) and shows the relative intensity of actual fluorescence in different concentrations.

The following method of obtaining the corrected fluorescence curves was used as a check upon the first, the final results being obtained by a graphical rather than a mathematical procedure.

The apparatus was set up as before, except that the light exciting fluorescence, instead of striking the whole face of the glass, was allowed to strike only a vertical section 1 mm. in width. The side of the cell next to the exciting light S' was covered with a black paper screen having a vertical opening 1 mm. wide, through which light was admitted. This opening was set at different distances from the end of the cell and the fluorescence intensity was measured for three or four different positions. In order to make possible accurate measurements of the distance from the edge of the glass, a scale was etched upon the face of the cell just above the level of the collimator slit.

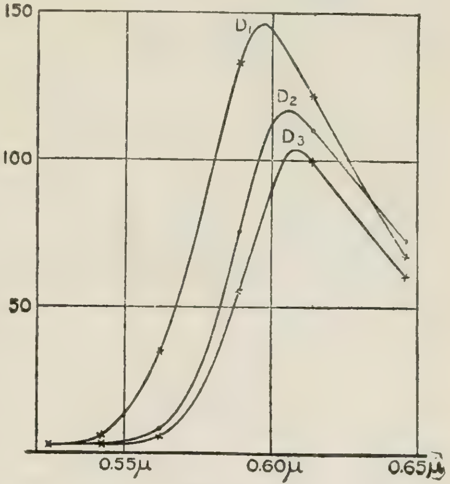

Fig. 34.

Observed fluorescence produced by light from 1 mm. section passing through different thicknesses of solution. Thickness of $D_1 = 1$ mm.; of $D_2 = 1$ cm.; of $D_3 = 2$ cm.

The effect of absorption upon the position of the maximum of the fluorescence spectrum is well shown in Fig. 34, in which the three curves were taken with the opening at different distances from the face of the cell.

In order to correct for absorption, curves similar to those shown in Figs. 35 and 36 were plotted for each solution. These curves show the variation in the intensity of the fluorescent light with the thickness of the liquid through which the light passes. From the intercept of one of these curves upon the *y* axis the intensity of fluorescence can be found when the thickness becomes zero. In such a case there is no absorption. The error of extrapolation was reduced to a minimum by taking one point very close to the edge of the glass.

The corrected values of fluorescence intensity thus obtained were used in plotting the accompanying fluorescence curve in Fig. 36. The same procedure was followed in the case of each solution.

The observations and results obtained by this graphical method are given in Table 10. The corrected fluorescence spectra obtained in this way are plotted together in Fig. 37, the vertical scale being such that values for wave-length 0.589 μ are the same as the values for the corresponding concentration in Fig. 32.

A comparison of the curves of Figs. 32 and 37 shows that the results obtained by the two methods are the same. The typical fluorescence curves are all similar in form and the position of maximum fluorescence (about 0.595 μ) remains constant for all dilutions. The shift in the observed fluoresence maximum is therefore due entirely to absorption.

This fixed position of maximum fluorescence seems to be consistent with the theory of ionization. According to Buckingham, ions may have some of the same optical properties as other substances and fluorescence is one of these properties. If only the ions fluoresce the position of maximum fluorescence would evidently remain constant whether the material of the solution were all ionized or not.

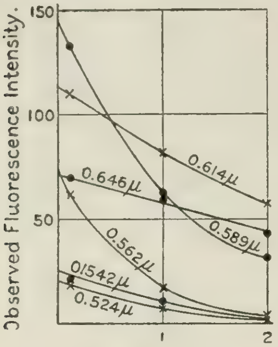

Fig. 35.

Variation in intensity of observed fluorescence from 1 mm. section transmitted through different thicknesses of solution.

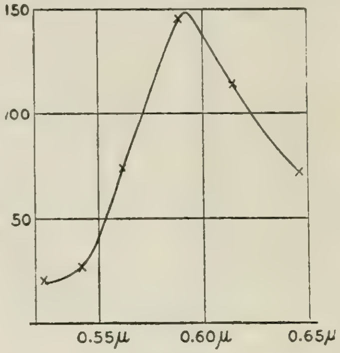

Fig. 36.

Fluorescence corrected for absorption by graphical method. Concentration = ⅛.

This fixed position of maximum fluorescence is also consistent with the theory suggested in Chapter I,[1] that fluorescence is caused by an unusual kind of dissociation similar to that produced in a gas by the action of Roentgen rays. That part of the solution which, during the process of change, produces fluorescence does not give evidence of any effect due to material not dissociated beyond that of absorption.

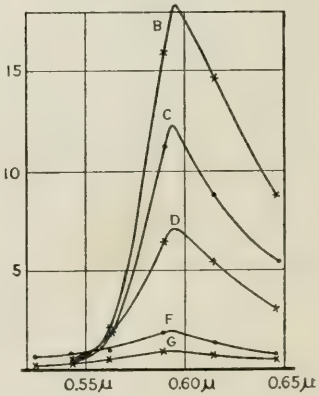

Fig. 37.

Fluorescence curves corrected for absorption by graphical method. Vertical scale same as for Fig. 32.

SUMMARY.

The results of the above investigation upon resorufin, as a typical fluorescent substance, taken in connection with the work of B. Walter and with the experiments described in Chapter I, seem to establish the truth of the following statements:

1. Fluorescent solutions are optically perfect substances, *i. e.*, they obey Lambert's law.
2. Beer's law, *i. e.*, that increase of concentration is equivalent to increase in thickness, is true for dilute but not for concentrated solutions.
3. A change in the concentration of a fluorescent solution has no effect upon the typical fluorescence spectrum.

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[1] Nichols and Merritt, Physical Review, XIX, No. 1, 1904; XXII, No. 5, 1906.

Table 10.

Observed fluorescence of section 1 mm. wide from which light is transmitted through different thickness of solution. The column marked 0 thickness gives fluorescence intensity corrected for absorption by graphical method, *i. e.*, by extrapolation from curves similar to those in Fig. 35.

λ	Concentration $\frac{1}{2}$.				Concentration $\frac{1}{4}$.			
	1.5 mm.	5 mm.	1 cm.	0	1.5 mm.	5 mm.	1 cm.	0
0.524μ	1.75	....	1.1	1.5				
.542	2.52	1.6	1.2	2	2.83	2.1	1.3	3
.562	14.3	3	1.95	12.5	9.07	4.1	2.32	13.8
.589	66.2	41.5	29.6	114	71.4	45.9	21.4	103
.614	94.5	70.7	61.2	103	88.1	73.7	64.6	95
.646	42.4	42	42.5	43	51.4	48.7	54.3	52.3

λ	Concentration $\frac{1}{8}$.				Concentration $\frac{1}{16}$.			
	1.5 mm.	5 mm.	1 cm.	0	1 mm.	1 cm.	2 cm.	0
0.524μ	2.65	2	1.73	2.5	....	2.83	3	3.5
.542	3.9	2	2.66	4	5.92	2.97	2.83	8
.562	34.15	12.1	7.52	50	34.8	8.62	5.56	42
.589	96	69.7	49.5	109	132	75.9	55.4	144
.6	102	79.5	63.3	117				
.614	79.72	68.4	56.5	90	121	110	99.6	124
.646	34.7	33.6	31	36	67.3	72.7	60.3	70

λ	Concentration $\frac{1}{64}$.				Concentration $\frac{1}{128}$.			
	1.5 mm.	5 mm.	1 cm.	0	1.5 mm.	5 mm.	1 cm.	0
0.508μ	3.47	3.81	3	4				
.524	4.83	3.75	3.75	4	4.17	4.47	3.45	4.5
.542	6.16	4.9	4.23	7	6.52	6.1	5.33	6.8
.562	62	38.5	25.5	76	25.2	23.7	17	26
.589	146	138	125	150	49.2	49.5	47.4	49.5
.614	110	105	96.1	113	39.7	37.7	38.3	39.5
.646	58.1	50.2	31.7	60	27.8	25	27.5	28

CHAPTER III.

THE LUMINESCENCE OF SIDOT BLENDE.[1]

Among the substances whose luminescence is sufficiently bright for spectrophotometric study, Sidot blende or phosphorescent zinc sulphide seems especially well suited to bring out the relationships that doubtless exist between different types of luminescence; for not only is this substance excited to luminescence by all known exciting agents—light, Roentgen rays, radium rays, cathode rays, etc.—but the stimulating effect of heat and the property possessed by the red and infra-red rays of suppressing phosphorescence are exhibited in unusual degree. It is for this reason that we have chosen this substance for spectrophotometric study.

The material used in these experiments was in the form of a screen, of the kind frequently used in exhibiting the properties of radium and for numerous experiments in which it is desirable to have a fluorescent substance in convenient form. The experimental methods were similar to those described in Chapters I and II, a Lummer-Brodhun spectrophotometer, with an acetylene flame as a comparison source, being used to measure the intensity in different parts of the luminescence spectrum. In certain portions of the work special devices were required which will be described in their proper place.

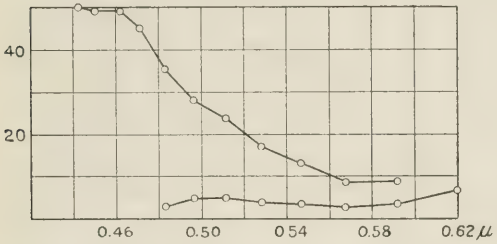

Fig. 38.

The uppercurve shows the luminescence spectrum of Sidot blende during excitation by Roentgen rays. The lower curve shows the phosphorescence 5 seconds after excitation.

LUMINESCENCE EXCITED BY ROENTGEN RAYS.

The screen was placed in front of the collimator slit of the spectrophotometer at a distance of only a few centimeters, while the Queen self-regulating tube used for excitation was about 20 cm. behind the screen. Roentgen rays of moderate "hardness" were used. No systematic experiments to determine the effect of varying hardness upon the form of the luminescence spectrum have yet been made, but a few preliminary tests indicate that the effect is not great. Corrections due to fluorescence excited in the glass of the spectrophotometer, which we had at first thought would be necessary, were found to be negligible.

The upper curve in Fig. 38 shows the luminescence spectrum observed during excitation, while the lower curve shows the distribution of intensity

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[1] An account of the experiments described in this chapter was presented to the American Physical Society at the Philadelphia meeting December 30, 1904. Physical Review, XXI, p. 247; XXII, p. 279; XXIII, p. 37.

in the phosphorescence spectrum, observed 5 seconds after excitation had ceased. Owing to the weakness of the phosphorescence excited by Roentgen rays, the latter curve was determined with some difficulty, the readings at the red end of the spectrum being especially uncertain. The indications of a second maximum in the phosphorescence spectrum at 0.62 μ or beyond are therefore not to be regarded as entirely trustworthy.

PHOTO-LUMINESCENCE DURING EXCITATION.

In the experiments upon photo-luminescence during excitation the carbon arc was first used as an exciting source. The arrangement of apparatus is shown in Fig. 39. The zinc sulphide screen was placed in a light-tight box *B*, and the exciting light from an arc *A*, after dispersion by the prism *P*, entered the box through an opening at the left. A second opening in *B* allowed the fluorescence light to enter the slit of the Lummer-Brodhun spectrophotometer S_1. The comparison source was an acetylene flame *F*, whose rays were reflected into the comparison slit by the block of magnesium carbonate, *M*. The second spectrophotometer S_2 and the shutter *C* were used in later experiments on phosphorescence, but not in the experiments now considered.

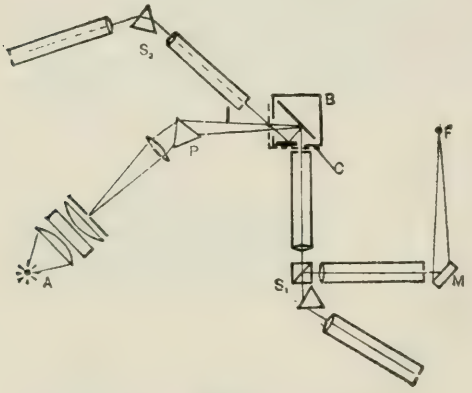

Fig. 39.

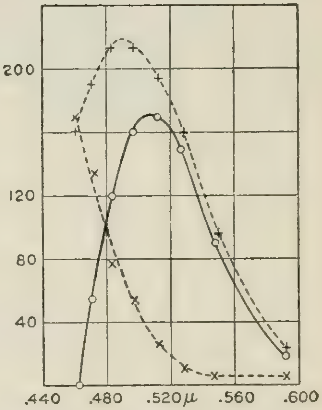

Fig. 40.

Luminescence spectrum of Sidot blende during excitation by the violet bands in the arc.

Luminescence was excited only by the rays at the violet end of the arc spectrum, and especially in the region of the violet bands. It is to be noted that on account of the absorption of the glass prism and lenses the spectrum extended only a short distance into the ultra-violet.

Observations taken to determine the luminescence spectrum when the zinc sulphide screen was excited by the violet bands of the arc are plotted in Fig. 40. Owing to the impurity of the exciting spectrum a certain amount of blue and green light reached the screen even when the attempt was made to excite by violet only. Since this stray light was in part reflected into the slit of the spectrophotometer with the luminescence light of the same color, it was necessary to make a correction to remove the error due to this cause. The correction was determined by replacing the zinc sulphide screen by a block of magnesium carbonate, whose surface was of approximately the same color and roughness as that of the fluorescent screen, and by measuring the light received from this block at different points throughout the spectrum. The results of such a series of measurements is shown in the lower broken line in the figure. It will be noticed that the correction is inappreciable for the longer wave-lengths, but becomes important in the violet. The upper broken line in Fig. 40 shows the intensity of the light reaching the spectrophotometer from the zinc sulphide screen, being the combined effect of luminescence and reflected light; and the heavy curve, obtained by subtracting the ordinates of the lower curve from those of the upper, shows the corrected luminescence spectrum during excitation.

The curves in Fig. 40, like those shown in the previous chapters, are expressed in terms of the acetylene flame as a standard. In other words, each ordinate represents the ratio of the intensity of the luminescence light, of the particular wave-length considered, to the intensity of the light of the same wave-length from the acetylene flame; the curves are not energy curves.[1]

When the screen was excited by the arc as described above no trace of the violet luminescence, which had been so prominent with Roentgen-ray excitation, could be observed. It seemed not unlikely, however, that the absence of the violet band was due to the fact that the ultra-violet rays suitable for exciting it had been removed from the light from the arc by the glass prism and lenses of the dispersing system. We therefore rearranged the apparatus so as to use a quartz prism and quartz lenses, while a spark between metal terminals was substituted for the arc. Since the excitation in the region studied was solely by ultra-violet rays that were incapable of passing through glass, it was a simple matter to test for errors due an impure spectrum, or to any other source of stray light, by inserting a piece of glass in the path of the exciting rays. This test showed that stray light was in no case present in appreciable amount.

This ultra-violet excitation developed strong fluorescence in the extreme violet, similar in color to that produced by Roentgen rays. But the green band that had been excited by the visible rays of the arc was relatively very weak. In spite of its faintness, however, the presence of the green band could be readily detected, for while the violet luminescence died out almost immediately when excitation ceased, the green persisted as a slowly decaying phosphorescence observable for several minutes.

The similarity between the effects of ultra-violet light and those of Roentgen rays as exciting sources is worthy of note. In each case the chief luminescence is in the extreme violet, and is of short duration. But in each case also this is accompanied by luminescence in the green, which is relatively faint but of long duration. As is illustrated in numerous other cases, the Roentgen rays, when comparable at all with rays of light, are rather to be compared with ultra-violet light than with the rays of the visible spectrum.

The agreement between the luminescence spectrum excited by Roentgen rays and that observed in the case of ultra-violet excitation is not exact.

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[1] For a description of a method of reducing such curves giving the distribution of energy in fluorescence spectra see Nichols and Merritt, Physical Review, xxx, p. 328; also Chapter XII of this memoir.

We are of the opinion that the difference is due to the fact that the violet luminescence does not consist of one band only, but of at least two, which are excited by Roentgen rays and ultra-violet light in different relative intensity. The matter will be made clear by reference to Fig. 41. Curve *I* shows the luminescence spectrum when ultra-violet rays from the iron spark were used for excitation. The rays used were those giving most intense luminescence, and did not lie much beyond the edge of the visible spectrum. The shape of this curve suggests that it is made up of two overlapping bands, one having a maximum not far from 0.48 μ, while the other has its maximum near 0.42 μ. In curve *II* the exciting light was at the extreme ultra end of the iron spectrum, and in curve *III* the magnesium lines near 0.33 μ were used in excitation. In these curves also there is every indication that the spectrum consists of at least two bands.

Unfortunately we have not been able to separate the bands more completely. It is to be remembered that the resolving power of a spectrophotometer is at the best small, and that in experiments of the kind here described the small intensity of the light studied prohibits the use of a narrow slit. Luminescence bands may sometimes be separated by a proper choice of the exciting light. In the case of Sidot blende the green band is very readily obtained alone by using the carbon bands of the arc for excitation. But the two violet bands in the luminescence of this substance are so close together that their regions of excitation appear to overlap throughout nearly their whole extent. The most that we were able to do was to show that ultra-violet rays of different wave-length produced different relative intensities in the two bands, as illustrated by curves *I* and *III* of Fig 41.

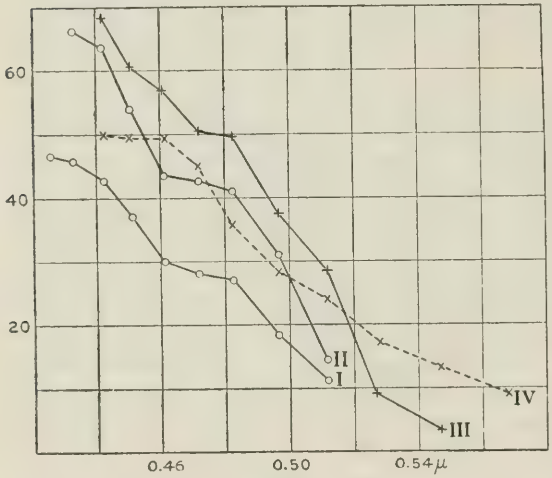

Fig. 41.

Fluorescence spectrum of Sidot blende when excited by the ultra-violet rays of the iron spark (curves *I* and *II*), by the ultra-violet of the magnesium spark (curve *III*), and by the Roentgen rays (curve *IV*).

The broken line, curve *IV* of Fig. 41, shows the luminescence spectrum excited by Roentgen rays. This is the same curve that appears in Fig. 38, and is introduced in Fig. 41 to facilitate the comparison of the effects of the ultra-violet light and Roentgen rays. It will be observed that each of the curves in Fig. 41 might well result from the superposition of three bands, whose maxima lie approximately at 0.42 μ, 0.48 μ and 0.51 μ. In the Roentgen-ray luminescence the green band is relatively stronger than in the case of excitation by ultra-violet light, while the band at 0.48 μ appears to be entirely absent. In the luminescence produced by the magnesium spark (curve *III*) the green band, while still observable, is not so strong as in curve *IV*, while the band at 0.48 μ is readily detected. Curves *I* and *II* (iron spark) show scarcely any trace of the green band, but the bands at 0.48 μ and at 0.42 μ are well marked.

FAILURE OF STOKES'S LAW.

As already stated, the green band is most brilliantly excited by the violet, although rays from all parts of the ultra-violet spectrum are also capable of producing a considerable effect. We thus see that there is the same general relation between the position of the luminescence spectrum and that of the exciting light as in the case of fluorescence. In all the cases of fluorescence thus far studied we have found that the two spectral regions overlap. It therefore seemed interesting to see whether the same is true in the present case.

To settle this point it was necessary to use in excitation a far purer spectrum than that employed in our other experiments with Sidot blende. The rather crude dispersing system shown in Fig. 39 was therefore replaced by a large spectrometer. A spectrum of the arc was thrown on the collimator slit by the aid of a prism and single lens, and after a second dispersion in the spectrometer, light reached the phosphorescent screen as a sharply focused band. Using a shutter described below so as to observe the phosphorescence immediately after the exciting light was cut off, and making observations with the unaided eye instead of with the spectrophotometer, it was found that phosphorescence was unquestionably present for exciting light lying between 0.470 μ and 0.497 μ. Since the phosphorescence spectrum can readily be followed beyond 0.46 μ there appears to be the same violation of Stokes's law in the phosphorescence of Sidot blende that we have previously found in the case of fluorescence.

THE PHOSPHORESCENCE SPECTRUM DURING DECAY.

Although the phosphorescence of Sidot blende can be detected in a dark room for several hours after excitation has ceased, it remains sufficiently bright for spectrophotometric measurement only for a few seconds. In order to determine the law of decay for different wave-lengths and especially to determine the change, if any, in the phosphorescence spectrum during decay, the following procedure was followed:

A shutter, shown by the broken line *C* in Fig. 39, and sliding upon vertical guides, was attached to the box containing the phosphorescent screen. When this shutter was raised it permitted the exciting light to enter the box, as in the experiments just described, but at the same time closed the opening in front of the collimator slit. When the shutter was dropped it first cut off the exciting light and then, a moment later, opened the window in front of the collimator. The observer was in this way protected from the brilliant luminescence produced during excitation, but was enabled to observe the phosphorescence immediately after excitation had ceased. The comparison slit being set to some suitable reading, the observer recorded upon a chronograph the instant when the two parts of the spectrophotometer field appeared equally bright. By means of a suitable electric contact on the shutter a record was also made at the time when the exciting light was cut off. In this way the time required for the phosphorescent light to fall from its initial value to any given final value could be conveniently measured.

The determination of the instant when the rapidly changing phosphorescence became equal to the constant comparison light would at first appear to be a difficult observation, and one not capable of great accuracy. As a matter of fact these observations were fully as reliable as ordinary spectrophotometric settings, and at these low intensities far less trying to the eye.

The most serious difficulty encountered in these measurements arose from the unsteadiness of the exciting light. When constancy is essential the arc, even under the best of conditions, leaves much to be desired. After numerous unsuccessful attempts to obtain steady conditions we abandoned all special efforts to keep the excitation constant, and arranged to make observations only when the exciting light, either by adjustment or by accidental fluctuation, had reached a certain definite intensity. In order to accomplish this a second spectrophotometer (S_2 in Fig. 39) was used. Light from the luminescent screen was thrown into the collimator by means of a mirror as shown in the figure. The comparison light came from the acetylene flame F after reflection from a mirror and a block of magnesium carbonate not shown in the figure. One observer at the eyepiece of S_2 waited until the intensity of fluorescence reached such a value as to give equality of the two fields, and then, with suitable warning, dropped the shutter C. The second observer at S_1 then made a chronograph record as before described. Numerous determinations, often twenty or more, were made in this way for each point of the curves described below.

TABLE 11.

The observed time, in seconds, during which the phosphorescence fell from its initial intensity to the intensity at the top of the column.

Wave-length.	$I=100$.	$I=60$.	$I=30$.	$I=10$.	$I=5$.
0.461μ	....	....	....	0.458	....
.472	....	0.00	....	0.99	....
.483	0.00	.456	0.745	2.07	7.1
.497	.491	.95	1.63	3.13	....
.512	.502	1.00	1.80	3.41	10.4
.528	.290	0.682	1.49	2.91	....
.535	.00	....	....	....	....
.547	....	0.223	0.838	2.55	7.5
.553	....	0.00	....	....	....
.568	....	....	0.302	1.30	....
.572	....	....	0.00	....	....
.592	....	....	....	0.713	4.1

A preliminary set of measurements in which the duration of excitation was varied from 3 seconds to 30 seconds showed no variation in the time of decay. We conclude that the full effect of the exciting light is produced in less than 3 seconds.[1] In the subsequent experiments the duration of excitation was never less than 5 seconds.

The results of one set of determinations made in this way are given in Table 11 and are plotted in Fig. 42. In curve I the width of the comparison

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[1] Later experiments (see Chapter IV) show that the long-time phosphorescence of Sidot blende is very noticeably influenced by a change in the duration of excitation.

slit was kept at 100 divisions of its micrometer screw, and the time required for the phosphorescence of any given wave-length to fall from its initial value to this intensity was determined as described above. The curve is obtained by plotting wave-lengths as abscissas and times as ordinates. In curve *II* the width of the comparison slit was 60 divisions; in curve *III*, 30 divisions; and in curve *IV*, 10 divisions. Observations made at 5 divisions are not included on the plot. Points lying on the horizontal axis in Fig. 42 were located by determining by trial the wave-length for which there was a balance in the spectrophotometer the instant after dropping the shutter. These points are probably somewhat less reliable than the others.

The significance of these results is better shown by plotting them in a different way. In Fig. 43 wave-lengths are plotted as abscissas as before, but intensities, instead of times, are plotted as ordinates. Each curve in this figure shows the distribution of intensity in the phosphorescence spectrum at some definite time after the removal of the exciting light

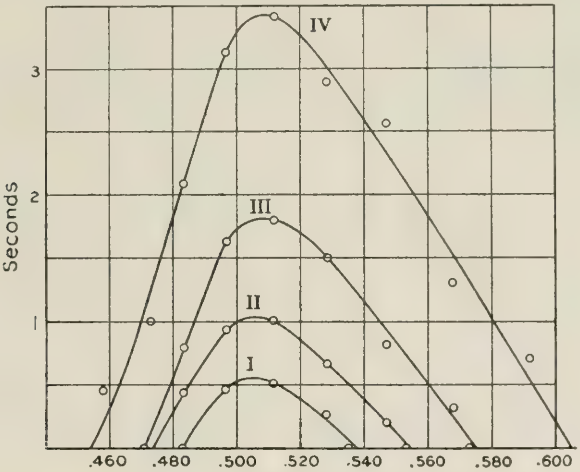

Fig. 42.

Curves showing the time required for the phosphorescence to fall from its initial intensity to a given final intensity. The final intensity is kept constant throughout each curve.

No curves have been plotted for intervals of more than 1.75 seconds after excitation had ceased, since our data furnished so few points for the later curves that their form would be largely a matter of conjecture.[1] As already stated, however, a curve of the type shown in Fig. 42 was determined for an intensity of 5 divisions. The maximum ordinate of this curve was 10.1 seconds and occurred at 0.506 μ; *i. e.*, at the same wave-length as in the case of the curves shown in 42. Comparison with Fig. 40 shows that the maximum of the luminescence spectrum during excitation also occurs at this wave-length. In the case of the green band of Sidot blende we conclude therefore that the maximum of the fluorescence spectrum occurs at the same wave-length as that of the phosphorescence spectrum,

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[1] In a series of observations of the kind recorded in Fig. 42 the number of points that could be located was limited both by the difficulty of maintaining constant conditions during the three or four hours of observation, and by the endurance of the observer's eye.

and that no change that could be detected by our apparatus occurs in the position of this maximum for 10 seconds after excitation has ceased.[1]

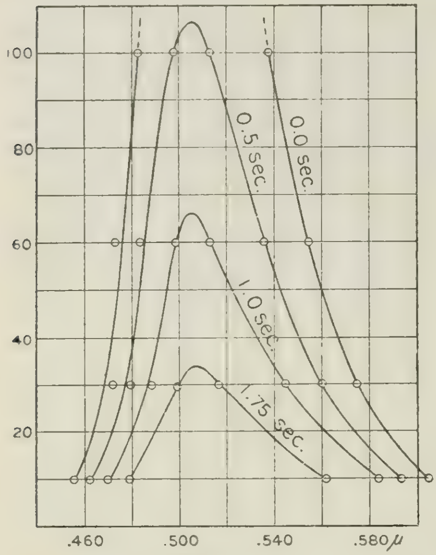

Fig. 43.

Phosphorescence spectrum of Sidot blende at different times after removal of the exciting light.

Fig. 43 also shows that if any change occurs in the form of the phosphorescence spectrum during decay, this change is extremely small. In other words, the different wave-lengths of the phosphorescence spectrum decay at the same rate. Table 12 will show to what extent this conclusion is justified by the data. Each column of this table refers to the wave-length stated at the top, and in it are tabulated the intensities for this wave-length at different intervals after the end of excitation, these intensities being expressed in terms of the intensity at the end of 1.75 seconds as unity. If the phosphorescence spectrum remains absolutely unaltered during decay, all the numbers in this table that lie in a given horizontal line should be equal.

The numbers in Table 12 corresponding to 0.0 second are uncertain; first, because the observations by which the initial phosphorescence was determined were themselves especially uncertain; and second, because the steepness of the curve (Fig. 43) in the neighborhood of 0.48 μ and 0.54 μ would cause a slight change in the manner of plotting to produce a large change in the ordinates at these wave-lengths. If the ratios tabulated for 0.0 second are left out of consideration, the agreement between the remaining ratios, at 0.5 second and 1.0 second, is as close as could be expected. We conclude that, although there is some indication of more rapid decay at the ultra edge of the phosphorescence spectrum, the probability is that all parts of the spectrum decay at the same rate, and that the form of the phosphorescence spectrum remains unchanged.

TABLE 12.

Intensity of phosphorescence at different intervals after excitation had ceased, expressed in terms of the intensity at the end of 1.75 sec.

	0.48μ	0.50μ	0.52μ	0.54μ	0.56μ
0.0 sec.	7.8?	....	....	5.2	4.8
0.5 sec.	3.5	3.3	3.1	3.0	2.8
1.0 sec.	1.9	2.0	1.8	1.8	1.9
1.75 sec.	1.0	1.0	1.0	1.0	1.0

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[1] Studies of the phosphorescence spectrum of Sidot blende by a photographic method, which made it possible to determine the position of the maximum at various times up to 90 seconds after excitation had ceased and which confirm this conclusion and extend it, will be described in Chapter VIII.

While the result obtained in this one case is not sufficient to establish a general law, we are nevertheless of the opinion that the behavior of Sidot blende is typical, and that in no case of phosphorescence is there any change in the form of a band during decadence. In complex cases of phosphorescence we do not imply by this that the phosphorescence spectrum as a whole remains unchanged in form, but rather that the distribution of intensity in each band is unaltered. If the phosphorescence consists of several bands, it is to be expected that the different bands will decay at different rates. In fact Sidot blende itself furnishes an extreme illustration of this, for the violet bands die out in one or two tenths of a second, while the green band persists for hours.

Numerous cases in which the color of a phosphorescent substance seems to change as the phosphorescence dies out at first appear to contradict this view. We think, however, that all cases of this kind may be shown to belong to one of the two following classes:

1. Cases of real color change; for example, anisic acid at low temperatures, where the phosphorescence changes from blue to greenish yellow.[1] Such cases are probably due to the presence in the luminescence spectrum of several phosphorescence bands, which decay at different rates. In the case of anisic acid the results would be explained by the presence of a brilliant but rapidly decaying band in the blue, and a persistent band of smaller initial intensity in the yellow.

2. Cases where the apparent change in color is due to the fact that the color sense in the eye is either weak or entirely absent at low intensities. At very low intensities all colors appear to the eye as gray. However brilliant may be the color of the phosphorescence light initially, it loses this color and changes to a gray or faint white as it becomes fainter. But such a change as this is in the retina, and does not indicate any change in the phosphorescence spectrum.

It is interesting to note that attention was called to both of these causes of change of color during decay by the elder Becquerel.[2]

The data of Table 11 might also be used to study the law of decay of phosphorescence, *i. e.*, the relation between intensity and time. More reliable results are obtained, however, by studying one wave-length at a time, since the data necessary for plotting a decay curve may in this case be obtained more quickly and are, therefore, less liable to error due to fluctuating conditions. Measurements of phosphorescence spectra during decadence, in the case of other substances, are described in Chapters IV and VII.

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[1] Nichols and Merritt, Physical Review, 18, p. 355, 1904.
[2] Ed. Becquerel, Comptes Rendus, 49, p. 27, 1859; Ann. de Chimie et de Physique, series 4, 62, p. 20, 1861.

CHAPTER IV.

THE DECAY OF PHOSPHORESCENCE IN SIDOT BLENDE AND CERTAIN OTHER SUBSTANCES.[1]

The decay of phosphorescence was first studied by E. Becquerel.[2] In the case of short-duration phosphorescence the phosphoroscope was used for this purpose and the intensity of phosphorescence was measured for different speeds of the rotating disk. Becquerel regarded it as probable that the law of decay was of the form

$$I = I_0 e^{-at} \qquad (1)$$

and found that the observations were in fact fairly well represented by an exponential expression. In discussing these observations, however, Becquerel tacitly assumed that no appreciable time was required for the exciting rays to produce their full effect. Later investigations have shown that this assumption is not justified. Since a change in the speed of the phosphoroscope altered not only the time that elapsed between excitation and observation, but also the duration of exposure, it is probable, therefore, that the initial excitation was less at high speeds. Attention was directed to this point by E. Wiedemann and later by H. Becquerel, who states that a recomputation of the data shows a less satisfactory agreement with the exponential law than at first appeared.

For the long-time phosphorescence of the phosphorescent sulphides E. Becquerel proposed an empirical expression of the form

$$I^m(c+t) = cI_0{}^m \qquad (2)$$

For each of the seven substances tested this expression was found to show a fairly good agreement with the experimental results throughout a considerable range. In one case, namely, that of a calcium sulphide preparation giving an orange-red phosphorescence, the expression represented the observations with considerable accuracy throughout the whole range, the value of m being 0.5. But in most cases it was not possible to find values of m and c which would make the formula fit the experimental data for the whole time of decay. The values of m that suited the observations best lay between 0.5, for the calcium sulphide just mentioned, and 0.806 for another calcium sulphide having an orange-yellow phosphorescence.

The same empirical formula has since been very generally used, among others by Darwin[3] in 1881, and Ch. Henry[4] in 1892. The former worked with Balmain's paint and found the best value for m to be 0.86. It can not be said, however, that the experimental results were represented very accurately by the formula. The substance used by Henry was Sidot blende,

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[1] An account of the work described in this chapter was presented to the American Physical Society at the meeting held on Oct. 28, 1905. Physical Review, XXII, p. 279.

[2] Becquerel, "La Lumiere." See also Comptes Rendus, 51, p. 921, 1860, and Annales de Chimie et de Physique, series 4, 62, p. 5.

[3] Philosophical Magazine, 11, p. 209, 1881.

[4] Comptes Rendus, 115, p. 505, 1892.

several different samples of which were tested. Henry states that in the case of one specimen the results were represented by an exponential law (eq. 1) for 14 seconds, while other preparations obeyed the law

$$i^{0.5936}(t+27.18)=1647.5 \qquad (3)$$

Henry appears to have been convinced of the correctness of the latter law and proposed a new type of photometer which made use of the gradually decaying phosphorescence of Sidot blende in the measurement of faint sources of light.[1] While the fact that the constant in eq. (3) is given to five significant figures indicates an accuracy that is unusual in photometric measurements, the lack of experimental data in the paper referred to makes it difficult to form an independent opinion of the significance of the conclusions.

The decay of phosphorescence was considered from the theoretical standpoint by H. Becquerel[2] in 1891. Upon the assumption that the light emitted during phosphorescence was due to molecular vibrations set up by the action of the exciting light and afterwards gradually dying out, it was shown that the law of decay would be determined by the nature of the damping forces. If the vibrations meet with an opposing force proportioned to the speed it was shown that an exponential law of decay would result; while if the resistance is proportional to the square of the speed the law of decay would take the form

$$I=\frac{1}{(a+bt)^2} \qquad (4)$$

It will be noticed that the empirical law proposed by E. Becquerel reduces to (4) in case $m=0.5$.

In the case of a substance whose phosphorescence spectrum contains several bands Becquerel proposed the expression

$$I=\Sigma\frac{1}{(a+bt)^2} \qquad (5)$$

in which there is one term in the summation for each band. Upon testing this law with the data obtained by E. Becquerel for a calcium sulphide giving blue phosphorescence it was found that the results could be expressed by the use of two terms in the above series with great accuracy. The existence in the spectrum of this substance of two bands possessing independent properties could be demonstrated in various ways.

In the derivation of the law proposed by H. Becquerel the assumption is that the vibrations set up by the action of the exciting light continue during several minutes or even hours. This would imply either that the vibrating atoms or molecules exist during this time without collisions with other molecules, or else that such collisions are without effect upon the vibrations. Neither of the suppositions seems to us tenable. But the law nevertheless appears to be of very general application. We shall show later that the same law may be derived from entirely different theoretical considerations. (See Chapter XV.)

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[1] Comptes Rendus, 115, p. 602.

[2] Comptes Rendus, 113, p. 618, 1891.

In all of the experiments upon the decay of phosphorescence with which we are familiar it is the total light that has been measured; so far as we are aware no attempt has been made to determine the law of decay for different portions of the phosphorescence spectrum. This fact complicates the problem greatly, for in most cases of phosphorescence the spectrum consists of two or more bands, which, in general, decay at different rates. It can hardly be expected, therefore, that measurements of the total light will be found to obey a simple law. The difficulties resulting from the complexity of the luminescence spectrum were recognized by E. Becquerel and were several times mentioned in the course of his classic researches. In discussing his experiments on decay he suggested an expression of the form

$$I=Ae^{-\alpha t}+Be^{-\beta t}+\ \ldots \qquad (6)$$

for the intensity of the total phosphorescence, with one term for each band in the spectrum. But the difficulties of computation were such as to lead him to abandon this expression and to employ instead the empirical expression of eq. (2). Recognition of the fact that each band has its own rate of decay is also implied in the law proposed by H. Becquerel (eq. 4).

While it is possible to test the correctness of an expression of the form of (4) or (6) by comparison with measurements of total intensity, such a test is difficult, and can not be altogether satisfactory; for with an expression containing several terms the number of constants is so great that the law may be made to fit almost any data. It is clear that a much more severe test of any given law of decay may be obtained from experiments with a substance having only one band in its phosphorescence spectrum. The Sidot blende screen used by us in earlier experiments was found to have three bands in its luminescence spectrum. But since the two violet bands do not appreciably overlap the green band the spectrophotometer enables the behavior of the latter band alone to be conveniently studied. The matter is still further simplified by using the violet rays of the arc in excitation, since these rays, while they produce a brilliant green luminescence, are incapable of exciting either one of the violet bands.[1] In view of the brilliancy of the green band, its long duration, and the ease with which it may be isolated, this band seems well adapted to the study of the decay of phosphorescence.

EARLY STAGES IN THE DECAY OF PHOSPHORESCENCE IN SIDOT BLENDE.

Our previous experiments on Sidot blende have shown that in the case of the green band the phosphorescence spectrum shows no measurable change in form during the first 10 seconds of decay. In other words, the rate of decay is the same for all wave-lengths. To fix the behavior of the whole band it would be sufficient, therefore, to determine the law for a single wave-length. We have, however, made measurements at three different wave-lengths, namely, at 0.483 μ, 0.512 μ, and 0.547 μ. The first of these wave-lengths lies near the ultra edge of the band; the second is not far from the maximum; and the third is near the red edge.

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[1] See Chapter III of this memoir.

The methods of measurement were the same as those described in Chapter III. The experimental data obtained are contained in Tables 13, 14, 15. In each case it is the average of from ten to twenty observations that is recorded.

In the set of observations contained in Table 13 the curves for 0.547 μ, 0.483 μ, and 0.512 μ were determined during the forenoon in the order just stated. The data for 0.512 μ with weaker excitation were observed during the afternoon of the same day. The observations recorded in Table 14 were taken in a different manner, the measurements at a given intensity being made for each of the three wave-lengths in succession. The observations of December 13 (Table 15) were made in a similar manner. The first three curves of Table 13 are plotted in Fig. 44, while the second and fourth curves of this table are shown in Fig. 45.

TABLE 13. [Nov. 25.]

Time in seconds required for the phosphorescence to fall from its initial intensity to the intensity *I*. The computed values of *t* are derived by substitution in the following equations:

For $\lambda=0.483\mu$ $1/\sqrt{I}=0.102+0.059t$
$\lambda=0.512\mu$ $1/\sqrt{I}=0.074+0.045t$
$\lambda=0.547\mu$ $1/\sqrt{I}=0.096+0.055t$
$\lambda=0.512\mu$ (weaker excitation) $1/\sqrt{I}=0.092+0.052t$

I	$\lambda=0.483\mu$		$\lambda=0.512\mu$		$\lambda=0.547\mu$		$\lambda=0.512\mu$ Weaker excitation.	
	t sec. Obs.	*t* sec. Comp.	*t* sec. Obs.	*t* sec. Comp.	*t* sec. Obs.	*t* sec. Comp.	*t* sec. Obs.	*t* sec. Comp.
101	....	....	0.63	0.58	....	....	....	....
81	....	....	0.83	0.85	....	....	....	....
61	0.41	0.44	1.38	1.20	0.56	0.58	0.72	0.69
41	0.99	0.92	1.84	1.83	1.10	1.09	1.24	1.23
21	1.88	1.98	3.25	3.23	2.07	2.23	2.42	2.45
11	3.16	3.39	4.95	5.10	3.87	3.74	4.03	4.04
6	6.55	5.23	7.42	7.50	5.82	5.71	6.22	6.92

TABLE 14. [Dec. 10.]

Time in seconds required for the phosphorescence to fall to the intensity *I*. The computed values of *t* are derived by substitution in the following equations:

For $\lambda=0.512\mu$ $1/\sqrt{I}=0.078+0.034t$ $\lambda=0.547\mu$ $1/\sqrt{I}=0.104+0.042t$

I	$\lambda=0.483\mu$		$\lambda=0.512\mu$		$\lambda=0.547\mu$	
	t sec. Observed.	*t* sec. Computed.	*t* sec. Observed.	*t* sec. Computed.	*t* sec. Observed.	*t* sec. Computed.
81.4	0.60	....	1.06	0.98	0.30	0.22
61.4	0.77	....	1.35	1.49	0.55	0.62
31.4	2.40	....	2.98	3.02	1.83	1.84
11.4	4.13	....	6.47	6.46	4.62	4.58

TABLE 15. [Dec. 13.]

Time in seconds required for the phosphorescence to fall to the intensity I. The computed values of t are derived by substitution in the following equations:

$$\begin{aligned} \text{For } \lambda=0.483\mu \quad & 1/\sqrt{I}=0.104+0.070t \\ \lambda=0.512\mu \quad & 1/\sqrt{I}=0.094+0.046t \\ \lambda=0.547\mu \quad & 1/\sqrt{I}=0.118+0.070t \end{aligned}$$

I	$\lambda=0.483\mu$		$\lambda=0.512\mu$		$\lambda=0.547\mu$	
	t sec. Observed.	t sec. Computed.	t sec. Observed.	t sec. Computed.	t sec. Observed.	t sec. Computed.
81.4	....	....	0.45	0.37	....	....
61.4	0.45	0.36	0.69	0.74	0.25	0.14
31.4	1.06	1.08	....	....	0.88	0.87
21.4	1.46	1.61	2.60	2.67	1.30	1.40
11.4	2.78	2.76	4.48	4.44	2.61	2.55
7.4	4.46	3.80	5.97	6.00	4.58	3.57

The data of the preceding tables have been used to test the applicability of each of the several proposed laws of decay to the case of a single band. It was found that the results can be closely represented by an expression of the form given in eq. (4). To determine the constants a and b of this equation a convenient graphical method was employed, in which the values of $I / \sqrt{I}$ were plotted as ordinates and times as abcissæ. Since eq. (4) may be written in the form

$$\frac{1}{\sqrt{I}} = a+bt$$

the points located in this manner should lie on a straight line. A straight line having been drawn as nearly as possible through all the points, the slant of this line and its y intercept at once gave the values of b and a respectively. The values of a and b determined in this way are given in each of the tables, and the values of t computed from the above equation are tabulated for comparison with the times observed.

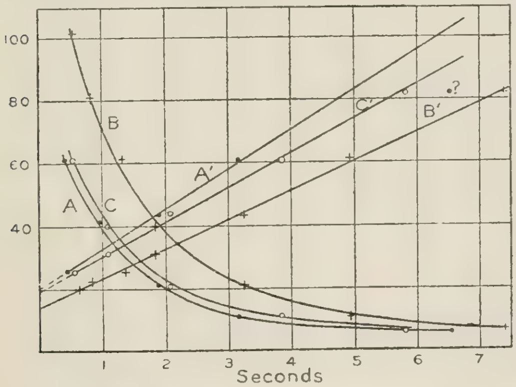

Fig. 44.

Curves A, B, and C show the decay in the phosphorescence of Sidot blende for the wave-length 0.483 μ, 0.512 μ, and 0.547 μ, respectively. The curves A', B', and C' are obtained from A, B, and C by plotting $I^{-\frac{1}{2}}$ instead of the intensity of phosphorescence, I.

In Figs. 44 and 45 the values of $I^{-\frac{1}{2}}$ have been plotted as described above. It will be noticed that in each case the points lie very nearly upon a straight line, and that there is nothing to indicate any systematic variation from linearity. In the case of one curve, namely, that for 0.483 μ in Table 14, the points located in this way did not lie even approximately on a straight line. This curve, therefore, does not have the form corresponding to eq. (4). But in the case of the other curves, including one taken at this same wave-length (Table 13), the agreement between the observed and computed values of t is satisfactory, the differences being only such as might well result from accidental errors. It seems probable, therefore, that the observations at 0.483 μ in Table 14 were subject to some unusual source of error.

In Fig. 44 it will be noticed that one point of the line A' (indicated by a question mark) falls below the line, *i. e.*, the observed time of decay was considerably greater than that computed from an assumed linear relation between $I^{-\frac{1}{2}}$ and t. Discrepancies of the same kind will be found for the smallest values of I in the first curve of Table 13 and for the first and last curves of Table 15. No such discrepancies are present in any of the four curves taken at 0.512 μ—*i. e.*, near the maximum of the phosphorescence spectrum. If these cases of disagreement between the observed and computed values of t are not due to accidental errors, they show the beginning of a systematic variation which will be dealt with at length in a later paragraph.

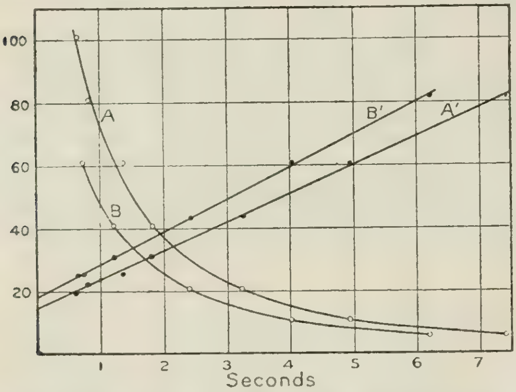

Fig. 45.

Curves A and B show the decay of phosphorescence at 0.512 μ for two different intensities of the exciting light. In the curves A' and B' $I^{-\frac{1}{2}}$ is plotted instead of the intensity I.

The theory discussed in Chapter XV leads us to expect that under ideally simple conditions the decay of phosphorescence should be in accordance with the equation

$$\frac{1}{\sqrt{I}} = a + bt$$

where

$$a = \frac{1}{n_0\sqrt{ka}} \qquad b = \sqrt{\frac{a}{k}}$$

It is to be remembered that if I refers to the intensity at some particular part of the phosphorescence spectrum, k must be regarded as a function of the wave-length.

The fact that the experiments indicate a linear relation between the time and $I^{-\frac{1}{2}}$ has already been pointed out, and reference to the tables on pages

54 and 55 shows that the differences between the computed and observed values of t, which are usually small, are entirely unsystematic. It is possible to test the law still further by considering the values of the constants a and b. Except in the case of the last curve of Table 13, the data refer to curves of decay for different wave-lengths, but with the same excitation. α and n_0 are therefore constant, while k depends upon the wave-length. It will be noticed that

$$\frac{a}{b} = \frac{1}{n_0\sqrt{k\alpha}}\cdot\sqrt{\frac{k}{\alpha}} = \frac{1}{n_0\alpha}$$

This quotient should therefore be a constant for all curves taken with the same excitation and under similar experimental conditions. The values of the ratio a/b for the three curves of Table 15 show considerable variation from equality, being 1.5, 2.0, and 1.7. The values of the ratio for the first three curves of Table 13 are 1.73, 1.75, and 1.65. In view of the difficulty of maintaining constant conditions in the experiments on phosphorescence the agreement between these three values is highly satisfactory. As already stated, the observations at 0.483 μ in Table 14, probably on account of some experimental error, can not be represented by the expression here considered, so that the value of a/b for this curve can not be determined. But for the curves taken at 0.512 μ and 0.547 μ (Table 14) the quotient a/b has the values 2.32 and 2.43, respectively. Here, too, the agreement is all that could be expected.[1] Our results therefore afford strong confirmation not only of the conclusion that all parts of the green band decay at the same rate, but also of the general theory of phosphorescence that we have used in deriving the law of decay.

The data permit still another test of the general theory, the result of which is less satisfactory. It will be remembered that in the case of the fourth curve of Table 13 the exciting light was less intense than that used with the other curve for 0.512 μ. The observations for the fourth curve were made on the same day as those for the second curve, and although the former were made in the afternoon and the latter in the forenoon, every attempt was made to keep the comparison source the same in the two cases and to have all the other experimental conditions as nearly as possible constant. If we compare the two curves for 0.512 μ in Table 13, we see that a and k have the same value for both, while n_0 is different. It would seem reasonable, however, to regard the constant b as independent of n_0. This constant should therefore have the same value for both curves; in other words, the straight lines obtained by plotting $I^{-\frac{1}{2}}$ should be parallel. As a matter of fact the values of b determined for the two curves are 0.045, for the second curve of Table 13, and 0.052 for the fourth. The fact that the two values are unequal is shown in Fig. 45 by the lack of parallelism of the two lines A' and B'.

Both the theory of Becquerel and the simple theory first discussed in Chapter XV fail to explain this result; which, however, is in accord with the modified theory of Wiedemann and Schmidt discussed in the latter part of Chapter XV.

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[1] There is no reason why the value a/b for Table 13 should be the same as those for Table 14 or 15, since the observations were made several weeks apart, and with no attempt to keep the intensity of the comparison source the same in the different cases.

THE STUDY OF PHOSPHORESCENCE IN SIDOT BLENDE AND CERTAIN OTHER SUBSTANCES DURING THE WHOLE PERIOD OF DECAY.

In the experiments just described the phosphorescence of Sidot blende was followed by the spectrophotometer for about 10 seconds after the cessation of excitation. At the end of this period the intensity of phosphorescence had fallen to about 4 per cent of its original value. Although it was possible to see the phosphorescent light in the spectrophotometer for a much longer period than this, the extreme faintness of the field made accurate measurements out of the question. In attempting to determine the law of decay throughout a wider range we have therefore been compelled to abandon the use of the spectrophotometer and to measure the total light.

Measurements of the total intensity do not, in general, afford a satisfactory means of determining the law of decay of phosphorescence, since, as has already been pointed out, the phosphorescence spectrum usually contains two or more bands, which decay at different rates. We have already referred to the difficulties that are met with in interpreting the results of such measurements. In the case of Sidot blende the conditions are, however, relatively simple, for the phosphorescence of the green band is so much more prominent, both in duration and in intensity, than that of the violet bands that the presence of these does not appreciably affect the total intensity. Measurements of the total phosphorescence of Sidot blende are therefore practically measurements of the intensity of the green band only. If all parts of this band decay at the same rate, measurements of total intensity will give the same results as measurements taken at some particular portion of the band. Our earlier observations have shown that all parts of the green band of Sidot blende do decay at the same rate for at least 10 seconds. It seems not unlikely, therefore, that this equality of rates will be maintained.

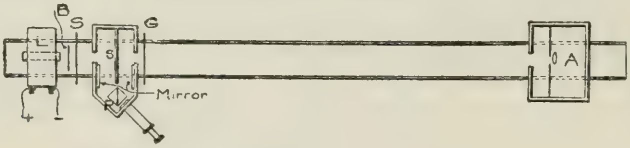

Fig. 46.

Although the present section deals chiefly with the phosphorescence of Sidot blende, the results obtained in the study of several other substances are also included.

EXPERIMENTAL METHOD.

The apparatus used is shown in Fig. 46. The white screen was removed from a Lummer-Brodhun photometer and the Sidot blende screen, *s*, was put in its place, the active surface of the screen being toward the left. The screen was usually excited by a Lummer mercury lamp, *L*, of the "end on" form. In some instances the carbon arc, and in other cases the spectrum of the carbon arc, was used for excitation. The exciting light could be cut off by means of a shutter, *S*, which at the same time made a record on a chronograph. When the mercury lamp was used in excitation a piece of blue glass, *B*, was placed between the lamp and the screen, so that only the violet lines in the spectrum were used.

The right-hand side of the screen was of white paper and could be illuminated by means of the acetylene lamp *A*. Two pieces of green glass, *G*, served to produce a sufficient color match. The acetylene flame *A* was in a metal box, and the light used emerged from a small opening immediately in front of the central part of the flame. Small changes in pressure were therefore without effect upon the intensity of this comparison source.

The procedure in taking observations was as follows:

One observer, with his eyes suitably protected from stray light, watched the decay of the phosphorescence after the shutter had been closed, and recorded by means of a key the instant at which the phosphorescent light and the comparison field were equal. The second observer then shifted the position of the comparison flame *A* to a slightly greater distance from the photometer, and the time when equality was again reached was recorded as before. In this way it was often possible to get as many as 15 points on the curve of decay, although a smaller number than this was more usual.

EXPERIMENTS WITH SIDOT BLENDE.

In preliminary experiments the light from the carbon arc was used in excitation. It was thought that simpler conditions would be obtained if exciting light having only a small range of wave-lengths was used, and a spectrum of the arc was therefore formed, the violet end of which was used for excitation. The gain in the intensity of phosphorescence which resulted from cutting off the red and infra-red rays was very noticeable.

In our previous experiments with Sidot blende it was found that the decay of phosphorescence during the first 7 seconds was in accordance with the law

$$I = \frac{1}{(a+bt)^2}$$

so that upon plotting the curves with T and $I^{-\frac{1}{2}}$ as coordinates a straight line was obtained. Since the distance between the photometer screen and the acetylene flame is proportional to $I^{-\frac{1}{2}}$, it was convenient to plot the results of the present experiments in the same way.

The general character of the decay curves when plotted in this manner is exhibited by the curves of Fig. 47. The violet end of the carbon arc spectrum was used in excitation, and the duration of excitation was varied as indicated.

Inspection of Fig. 47 shows that while each curve starts as a line which is nearly straight in the neighborhood of the origin, it soon begins to bend over and ultimately changes into a second straight line having a different slant. This behavior is especially noticeable in the case of long exposures.

If phosphorescence is due to the recombination of ions that have been separated by the action of the exciting light, as assumed in the theory of Wiedemann and Schmidt, it appears that the coefficient of recombination does not remain constant during the whole period of decay. During the first 6 or 7 seconds this coefficient is practically constant, as was shown by the results of our previous experiments. A change then begins which continues for about 20 or 30 seconds, after which the curves indicate a new coefficient, smaller than before. This new coefficient, as is shown by the constant slant of the curves of Fig. 47, remains constant during the rest of the period of decay, or at least until the phosphorescence has become too faint to measure. Whatever theoretical interpretation of the curves is adopted it is clear that the decay of phosphorescence involves two distinct processes which merge into one another. In each of these the decay obeys the simple law already referred to, but the rate at which the phosphorescence dies out is greater in the first process than in the second.

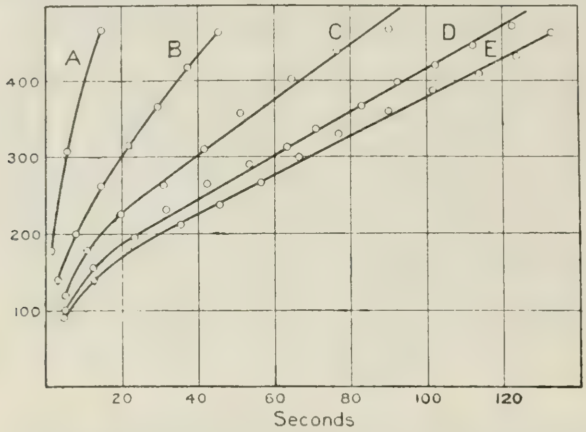

Fig. 47.

Effect of duration of excitation. Violet end of carbon-arc spectrum used in excitation. The curves were taken in the order indicated by the letters. The times of excitation were as follows: Curve *A*, 0.9.; *B*, 2.4 sec.; *C*, 4.5 sec.; *D*, 9.2 sec.; *E*, 17.5 sec.

It will be observed that the slant of the curve, for each of the two processes, is a function of the duration of excitation.

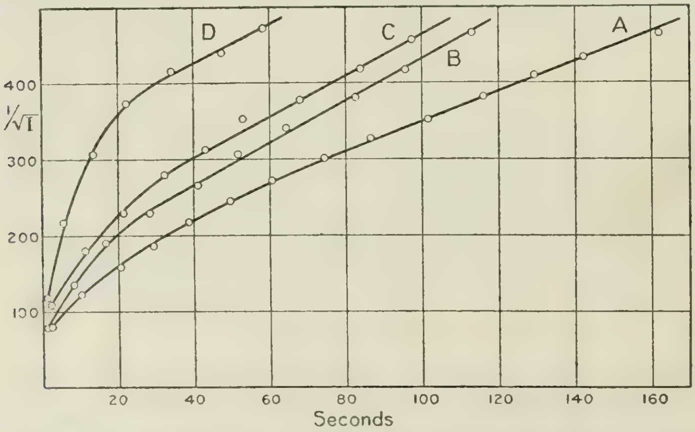

Fig. 48.

Effect of duration of excitation. Violet light of mercury arc used for excitation. The curves were taken in the order by the letter. The times of excitation were as follows: Curve *A*, 27 sec.; *B*, 10 sec.; *C*, 3.1 sec.; *D*, 1.2 sec.

In Fig. 48 is shown a series of curves taken under the same conditions as those of Fig. 47, except that the mercury arc was used in excitation instead of the violet end of the ordinary arc spectrum. One is immediately struck by the difference between the two sets of curves. In Fig. 48 there is a strong tendency toward parallelism in the parts of curves corresponding to the second process. In Fig. 47 no such tendency is observable.

We were at first inclined to ascribe this difference to the fact that different kinds of exciting rays had been used in the two cases; but the two sets of curves differ in another respect, namely, in the order in which the curves were taken. In the first case the curves of short excitation were taken first, while in the latter case the curves corresponding to long excitations were the first observed. It appeared possible that the difference in the form of the curves was due to this difference in sequence rather than to the difference in exciting light.

To test this matter the observations plotted in Fig. 49 were made. It will be noticed that the dotted curves are similar to those in Fig. 48, while the full curves are similar to those of Fig. 47. The mercury arc was used in excitation in all cases. But curves taken after the screen had been subjected to the long excitations corresponding to curves *C* and *D* differ widely from the curves taken with approximately the same excitation previous to *C* and *D*. A comparison of curves *A* and *E* illustrates this point, the the duration of exposure being exactly the same in each of these two cases.

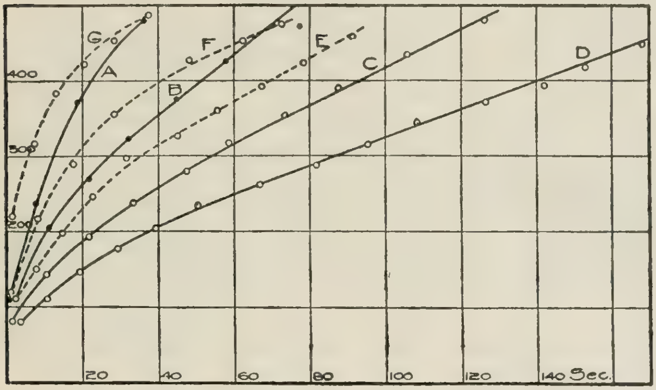

Fig. 49.

Effect of duration of excitation. Mercury arc. The curves were taken in the order indicated by the letters. The times of excitation were as follows: Curve *A*, 4.3 sec.; *B*, 8.2 sec.; *C*, 16.0 sec.; *D*, 56.0 sec.; *E*, 4.3 sec.; *F*, 1.4 sec.; *G*, 1.0 sec.

These results indicate that some change is produced in the phosphorescent material by the action of the exciting light, and that this changed condition persists for a considerable period after all visible phosphorescence has ceased. In other words, the effect of a given excitation in producing phosphorescence depends upon the previous history of the phosphorescent substance.

If the screen is allowed to rest in the dark for a number of hours this semi-permanent effect of exposure in part dies out. But rest alone does not restore the screen completely, even if continued for several days. The effect of rest was also found to be somewhat uncertain, being much greater on some occasions than on others.

Several methods of restoring the screen to a standard condition were tried. Heating the screen to the temperature of boiling water for several minutes and then cooling it again to the temperature of the room seemed effective. But this method required considerable time and has not been thoroughly tested. Cooling the screen to the temperature of liquid air and afterwards warming it gradually to the original temperature seemed to be without effect.

The well-known effect of the red and infra-red rays in suppressing the long-time phosphorescence of various substances led us to think that these rays might also prove effective as a means of restoring the screen to a standard condition. This conjecture proved to be correct, and exposure to the red and infra-red rays of a 50 c.p. lamp at a distance of about 20 cm. was found to be both convenient and satisfactory. A piece of ruby glass placed in front of the lamp served to remove the more refrangible rays. An exposure of a few seconds to the rays that passed through the ruby glass was sufficient to bring the screen into what seemed to be a definite standard condition. A longer exposure was, however, ordinarily used.

The changes produced by excitation and the effect of the red and infra-red rays are illustrated by the curves shown in Fig. 50. Curve *A* shows the behavior of the screen when exposed for 10 seconds after resting in the dark for 24 hours. Curve *B* is that corresponding to an exposure of 2 minutes; curve *C* was taken with an exposure of 10 seconds immediately after curve *B;* and curve *D*, also with an exposure of 10 seconds, was taken after the screen had been exposed to the red and infra-red rays for 4 minutes.[1]

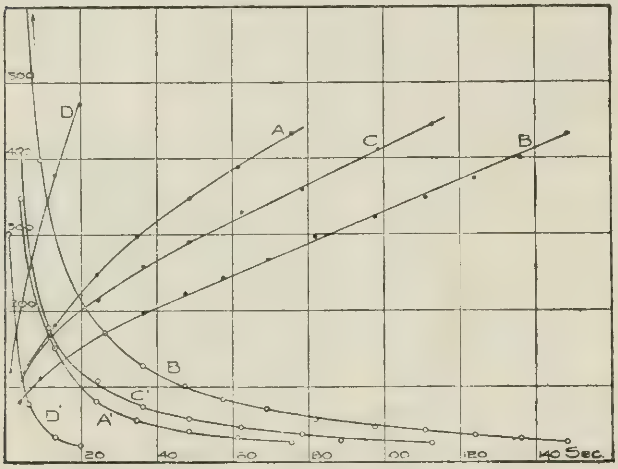

Fig. 50.—Illustrating relative effect of rest and exposure to infra red.

A, 10 sec. excitation after rest of 24 hours in the dark. *B*, 2 min. excitation.
C, 10 sec. excitation immediately after *B*.
D, 10 sec. excitation after exposure of 4 min. to infra-red from 50 candle-power lamp.
Curves *A'*, *B'*, *C'*, *D'* correspond to *A*, *B*, *C*, *D*, except that I is plotted in place of $I^{-\frac{1}{2}}$.

In some respects the behavior of the screen is analogous to the magnetic behavior of iron. When iron is magnetized a certain residual magnetization remains after the removal of the magnetizing force, and the effect produced by a subsequent magnetizing force depends upon the magnetic history of the specimen. Similarly some change is produced in Sidot blende by excitation which does not immediately disappear upon the removal of the exciting light, and which modifies the effect produced by subsequent excitation. The analogy is rendered more striking if this property of Sidot blende is exhibited in a different manner, as in Fig. 51. In the curve plotted in this figure the abscissa of each point shows the duration of excitation, while the ordinate gives the corresponding intensity of phosphorescence after 30 seconds decay. The resemblance of the curve to a hysteresis loop for iron is striking.

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[1] Experiments dealing with the effect of the infra-red rays during and after excitation will be found in Chapter V of this memoir.

It seems possible that the action of these rays in destroying the residual effect in the phosphorescent substance is similar to the effect of jarring or tapping in destroying the residual magnetism of a bar of iron. Ignorance of the existence of hysteresis would evidently lead to confusing results in the case of either of these two classes of phenomena. Our delay in recognizing the effect of previous history has in fact made it necessary for us to discard all of our earlier observations.

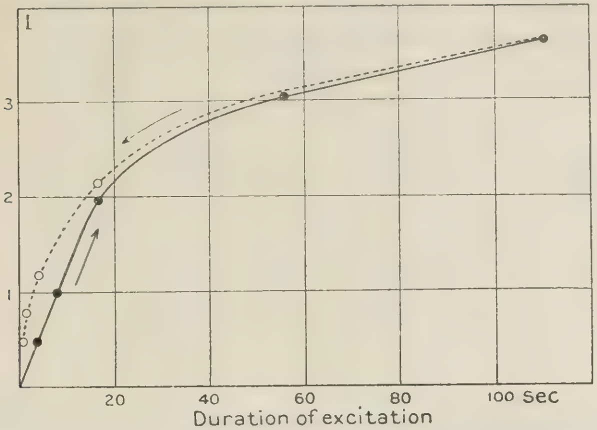

Fig. 51.

Hysteresis loop. Ordinates give the intensity of phosphorescence 30 seconds after the end of excitation. The curves from which these points were determined were observed in the order indicated by the arrows.

In our later work the screen was exposed to the red and infra-red rays as described for one minute before each exposure. With this precaution to avoid the effects of hysteresis the curves shown in Fig. 52 were taken to determine the effect of varying times of exposure.

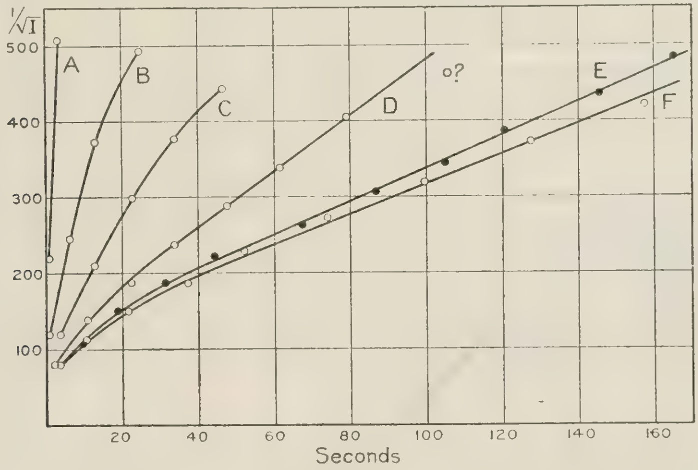

Fig. 52.

Effect of duration of excitation. Violet of mercury arc used for excitation. Screen exposed to infra-red for 1 minute before each curve. The times of excitation were as follows: Curve *A*, 1.2 sec.; *B*, 5.4 sec.; *C*, 12.0 sec.; *D*, 37 sec.; *E*, 60 sec.; *F*, 15 min.

Since our previous experiments have shown that the curves are accurately straight in the neighborhood of $t=0$, it is possible to determine the initial intensity of phosphorescence by prolonging the curves in each case until they strike the vertical axis. From the intercept thus determined, which is equal to $I_0^{-\frac{1}{2}}$, the initial intensity can be computed. From the results obtained in this way from the data shown in Fig. 52, curve *A* in Figs. 53 and 54 has been plotted. In these two figures *I* has been plotted instead of $I^{-\frac{1}{2}}$.

It will be noticed that the intensity of phosphorescence at first increases rapidly with increased duration of exposure, but that after an exposure of 2 or 3 minutes is reached there is little further change. The phosphorescence may be said to be saturated so far as the effect of duration of excitation is concerned. Not only is the initial intensity unaltered by longer excitation, but the form of the decay curve also remains constant, as is indicated by curves *a* and *b* in Fig. 53. (These curves correspond to curves *F* and *E* of Fig. 51.)

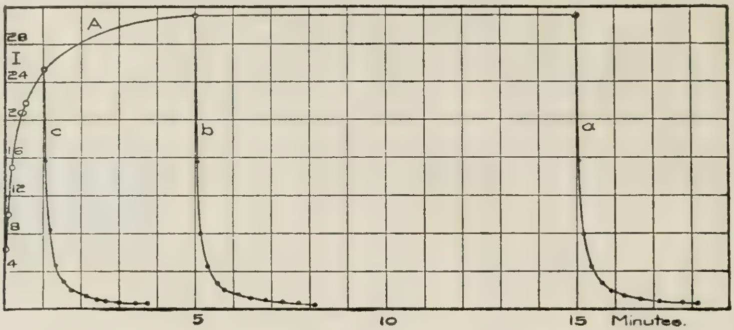

Fig. 53.

Effect of duration of excitation. Curve *A* shows initial intensity of phosphorescence (*I*) as a function of the time of excitation. Curves *a*, *b*, and *c* show the decay of phosphorescence after excitations of 15 minutes, 5 minutes, and 1 minute, respectively.

We have also studied to some extent the influence of the intensity of the exciting light upon the form of the decay curves. In order to vary the intensity of the exciting light several metal stops were prepared, which could be placed immediately in front of the mercury lamp. The apertures of these varied from 1 mm. in diameter to the full size of the mercury-lamp tube, namely, 15 mm. To determine the intensity of the exciting light corresponding to each of these the following photometric method was used: The phosphorescent screen was removed from the photometer and a piece of white cardboard was put in its place. This being illuminated

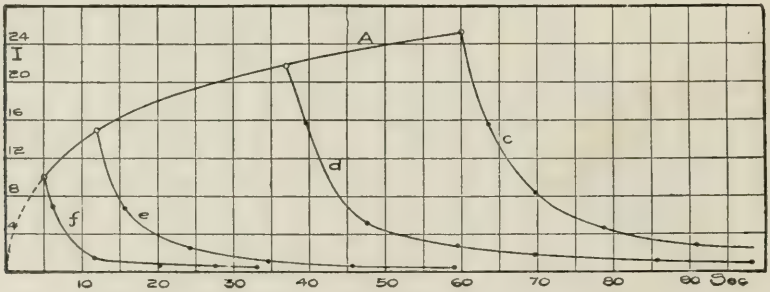

Fig. 54.

Effect of duration of excitation. A portion of the same curve shown in Fig. 54 plotted to a larger scale.

by the violet light from the mercury arc passing through the stop whose constant was to be determined, the intensity was measured by shifting the position of the comparison flame on the opposite side of the photometer. Suitable glass screens were used to equalize the colors on the two sides. To avoid errors resulting from the flickering of the mercury arc ten settings were made for each determination.

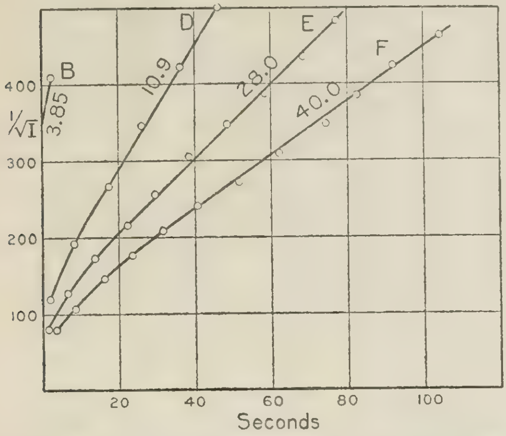

Fig. 55.

Effect of varying the intensity of the exciting light. Exposure in each case 20 seconds. The relative intensity of the exciting light is marked on each curve.

In Fig. 55 decay curves are shown for different intensities of the exciting light, the excitation in each case lasting for 20 seconds. In Figs. 56 and 57 similar sets of curves are shown for which the excitations were respectively 40 seconds and 2 minutes.

A study of these curves shows that there is some approach to intensity saturation; in other words, the intensity of phosphorescence is nearly proportional to the intensity of the exciting light for small values of the latter, but increases less rapidly than the excitation when the exciting light is strong. This point is well brought out by curve *A* in Fig. 58, in which the ordinates are proportional to the initial intensity of phosphorescence, I_0. The values of I_0 were determined from the data of Figs. 55, 56, and 57 by extrapolation, upon the assumption that the relation between

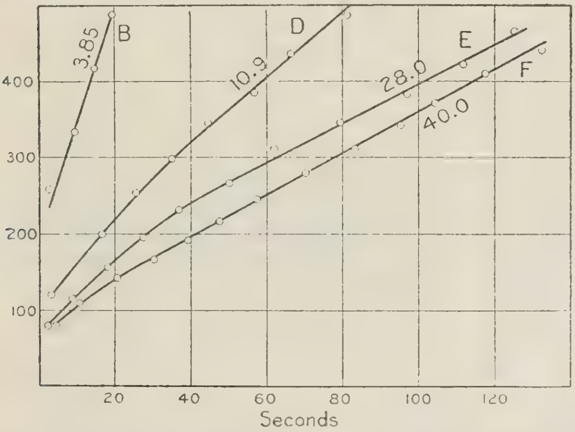

Fig. 56.

Effect of varying the intensity of the exciting light (as indicated on each curve). Exposure in each case 40 seconds.

t and $I^{-\frac{1}{2}}$ is linear for small values of t. Since the early portion of each decay curve is chiefly determined by the first two or three points, which are the most difficult to observe, the values plotted for I_0 are subject to considerable error. Curve *A* is nevertheless reasonably smooth and indicates nearly exact proportionality between intensity of excitation and initial phosphorescence. It is only with the most intense excitation used that saturation begins.

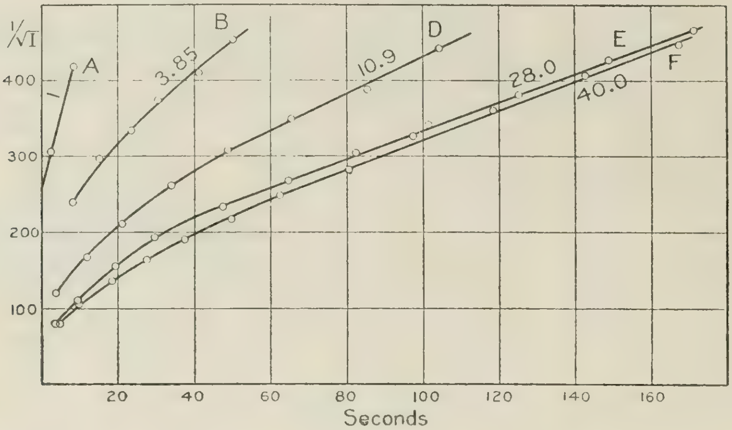

Fig. 57.

Effect of varying the intensity of the exciting light (as indicated on each curve). Exposure 2 minutes in each case.

It is to be observed that in most cases the values of I_0 that are computed from the data of Fig. 55 lie on the same curve as those obtained from the data of Fig. 57. A well-marked difference is noticeable only in the case of the points corresponding to intense excitation. In other words, for weak excitations the intensity of the initial phosphorescence is the same after an exposure of 20 seconds as for 1 or 2 minutes. There at first appears to be a contradiction here to the results shown in Figs. 53 and 54. But while this may be due to the uncertainty in the values of I_0, it is readily explained upon the assumption that a weak excitation produces its full

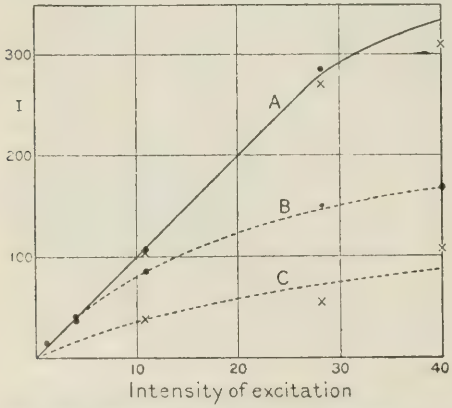

Fig. 58.

Effect of the intensity of the excitation upon the initial intensity of phosphorescence. The points marked by dots are for an exposure of 2 minutes; those indicated by crosses are for an exposure of 20 seconds. In curves *B* and *C* the ordinates show the intensity of phosphorescence 1 minute after excitation had ceased.

effect more promptly. The form of the curves shown in Figs. 53 and 54 is probably largely dependent upon the intensity of the exciting light.

The ordinates of curves *B* and *C* (Fig. 58) show the intensity of phosphorescence 1 minute after the exciting light was cut off. For curve *B* the exposure was 2 minutes, while for curve *C* the exposure was 20 seconds. The effect of duration of exposure is here well marked.

In the case of exposures lasting for several seconds or more the phenomena are manifestly complicated by the fact that the semi-permanent change, to which we have already referred, is taking place in the active substance during the time of excitation. It seemed probable that the relation between intensity of excitation and intensity of phosphorescence might prove simpler if the duration of excitation was reduced to a minimum. A series of curves was therefore taken with a spark as exciting source. Preliminary trials showed that the most intense excitation was furnished by discharging eight large jars through a spark gap about 2 cm. long with one cadmium terminal. The distance of the spark gap from the screen was varied from about 10 cm. to 35 cm. A single spark at 10 cm. distance gave an excitation approximately equivalent to 30 seconds exposure to the mercury arc.

Experiments with the practically instantaneous excitation produced by a single spark showed that the phosphorescence was proportional to the intensity of excitation, not merely initially but throughout the whole period of decay. In other words, it was possible to bring a decay curve determined with the spark at a distance d_2 into coincidence with the curve corresponding to the distance d_1 by multiplying each ordinate I_2 by the ratio d_2^2/d_1^2.

EXPERIMENTS WITH DIFFERENT PHOSPHORESCENT SUBSTANCES.

It is natural to inquire whether the complex phenomena exhibited by Sidot blende are peculiar to this particular material, or whether its behavior is typical of a large class of phosphorescent substances. In order to test this matter we have determined the decay curve under similar conditions with three other substances, namely, "Emanations-pulver,"[1] willemite, and Balmain's paint. Characteristic curves for these three substances, together with a representative curve for Sidot blende, are shown together in Fig. 59. It will be noticed that the curves are all of the same type. In each case the decay is at first rapid and apparently according to the same law that was found to hold during the early stages of decay in the case of Sidot blende. After 20 or 30 seconds the curves begin to bend, and finally become straight lines whose slant is less than that of the earlier part of the curve.

Upon plotting the data of E. Becquerel[2] in the same manner we find that in several cases the curves are of exactly the same type as those obtained by us. Three such curves are shown in Fig. 60. In fact, all the data recorded by Becquerel in his papers on this subject give curves which show the same general characteristics, although in several instances the curves are not so smooth as those shown in this figure.

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[1] Obtained from Leppin and Masche, who do not state the composition of the powder. The chief constituent is, however, zinc sulphide, so that the substance appears to be a modified form of Sidot blende. It is said to be especially sensitive to the influence of the radio-active emanations.

[2] Becquerel, La Lumière. Also Annales de Chimie et de Physique, Series 3, 62, 1861.

It is interesting to note also that the data of Darwin[1] on Balmain's paint give a curve similar to those obtained by us with this substance when plotted in the same way. Two decay curves taken by E. Wiedemann[2] with Balmain's paint also show the same characteristics.

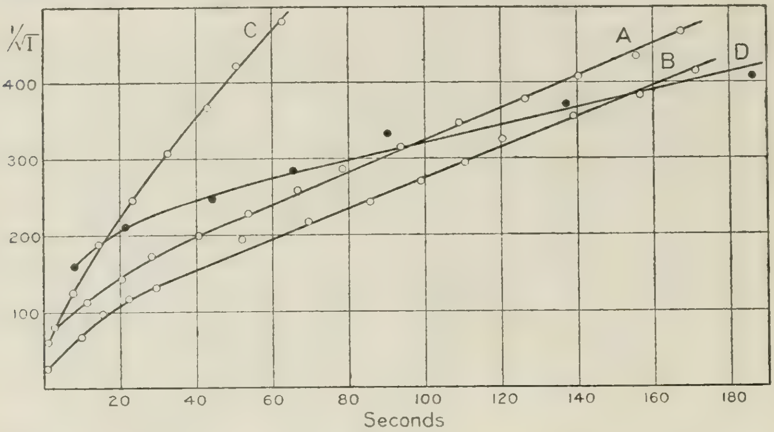

Fig. 59.

Typical decay curves for various substances. Curve *A*, Sidot blende; curve *B*, "Emanations-pulver;" curve *C*, Willemite; curve *D*, Balmain's paint.

It appears therefore that the decay curve for Sidot blende is similar in its main features to the curves obtained for a large number of other phosphorescent substances. In fact, we do not know of any case of long-time phosphorescence in solids which shows a different type of curve.

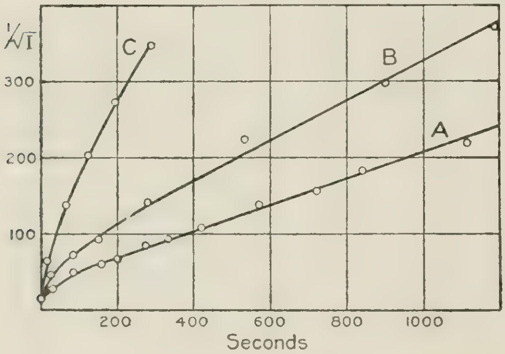

Fig. 60.

Decay curves plotted from the data of E. Becquerel. (Ann. de Chimie et de Physique, series 3, vol. 62, 1861.)

Curve *A*, Sulfure de calcium lumineux vert (2, p. 69).

Curve *B*, Sulfure de strontium lumineux vert (p. 71).

Curve *C*, Sulfure jaune-orange vif (p 68).

The peculiar behavior of Sidot blende which we have compared with magnetic hysteresis is also exhibited by willemite and Balmain's paint, as illustrated in Figs. 61 and 62. In each of these cases it is evident that the effect of a given excitation is dependent on the previous history of the substance. We have not yet had an opportunity to test this phenomenon in other substances.

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[1] Darwin, Philosophical Magazine, 11, p. 209, 1881.

[2] E. Wiedemann, Zur Mechanik der Leuchtens, Wied. Ann., 37, p. 177, 1889.

SUMMARY.

The most important points brought out by the experiments here described may be briefly stated as follows:

1. *Form of Decay Curve.*—The curve obtained by plotting the values of $I^{-\frac{1}{2}}$ as ordinates and the corresponding values of t as abscissas is a straight line for small values of t; it changes to a curve concave toward the axis of t as t increases; but for still larger values of t the relation between $I^{-\frac{1}{2}}$ and t is again linear, and remains so until I becomes too small to measure. In other words, the decay curve, when plotted in this way, consists of two straight portions which gradually merge into one another.

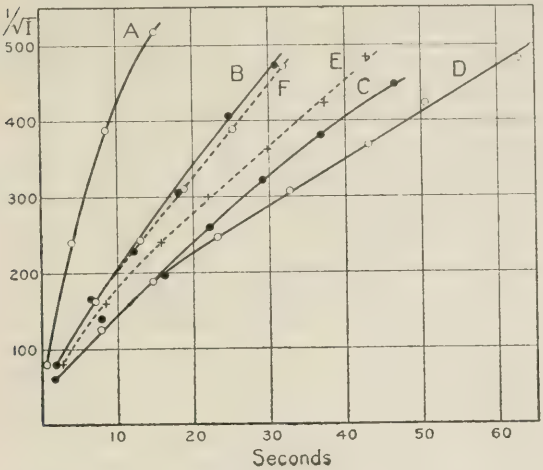

Fig. 61.—Willemite.

Excited by a spark between iron terminals. The curves were taken in the order indicated by the letters and with the excitations stated below:
Curve *A*, 0.7 sec.; *B*, 3.4 sec.; *C*, 9.0 sec.; *D*, 60.0 sec.; *E*, 3.9 sec.; *F*, 1.0 sec.

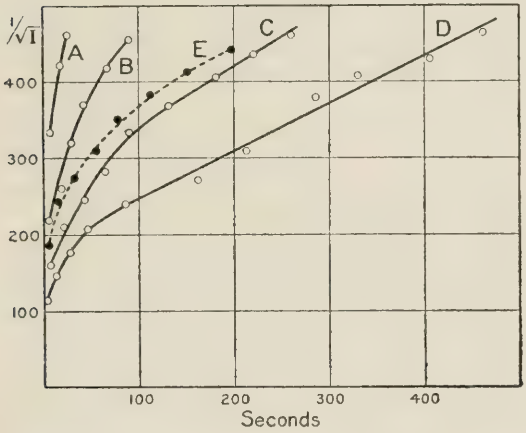

Fig. 62.—Balmain's paint.

The curves were taken in the order indicated by the letters, and with the following excitations:
Curve *A*, 5.9 sec.; *B*, 12.0 sec.; *C*, 26.0 sec.; *D*, 42.0 sec.; *E*, 6.4 sec.

2. *Effect of Duration and Intensity of Excitation.*—Not only the intensity of phosphorescence, but also the form of the decay curve, is dependent on the intensity and duration of excitation. The slant is altered in each of the straight parts of the curve by changing either of these two factors in the excitation.

3. *Hysteresis.*—The behavior of the phosphorescent substance with a given excitation depends upon its previous history. Some semi-permanent change is produced by excitation which persists for several hours, or even for several days, after visible phosphorescence has ceased.

4. *Effect of Red and Infra-red Rays.*—In the case of Sidot blende the semi-permanent condition produced by excitation may be destroyed and the screen restored to a standard state by brief exposure to the red and infra-red rays.

CHAPTER V.

THE INFLUENCE OF THE RED AND INFRA-RED RAYS UPON THE PHOTO-LUMINESCENCE OF SIDOT BLENDE.[1]

The effect of the red and infra-red rays in suppressing the phosphorescence of various substances has long been known,[2] and has frequently been utilized in the study of the infra-red spectrum. The effect is exhibited by Sidot blende more strongly perhaps than by any of the other phosphorescent sulphides. In Chapter IV we have called attention to another effect produced by the longer waves, namely, the restoration of a screen of Sidot blende, after the excitation and complete decay of phosphorescence, to a standard condition, so that the result of a subsequent excitation shall be unaffected by the previous history of the substance. While this new effect is doubtless connected in some way with that first mentioned, the nature of the relationship between the two is by no means clear. For this reason, and because of the bearing of the phenomena upon the general theory of luminescence, we have investigated the influence of the longer waves upon the luminescence of Sidot blende under a variety of different conditions.

The work naturally falls under several heads, as follows:

1. The effect upon the luminescence of Sidot blende of exposure to the longer waves *before* excitation.
2. The effect of the longer waves *during* excitation.
3. The effect of the longer waves *after* excitation, *i.e.*, during the decay of phosphorescence.
4. The influence upon the effect studied of the wave-length of the red and infra-red rays used.

THE EFFECT OF THE LONGER WAVES BEFORE EXCITATION.

Experiments described in the preceding chapter indicate that when Sidot blende is excited to luminescence "some change is produced in the material by the action of the exciting light, and that this change persists for a considerable period after a visible phosphorescence has ceased. In other words, the effect of a given excitation in producing phosphorescence depends upon the previous history of the phosphorescent substance. If the screen is allowed to rest in the dark for a number of hours this semi-permanent effect of exposure in part dies out. But rest alone does not restore the screen completely even if continued for several days." An exposure of a few seconds to the rays from a 50 c. p. lamp seen through ruby glass is, however, sufficient to restore the screen to what seems to be a definite standard condition.

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[1] The substance of this chapter essentially as here given appeared in the Physical Review, xxv, p. 362.

[2] References to the literature of the subject are given by Dahms, Annalen der Physik, 13, p. 425.

The phenomenon in question is illustrated by the curves of Fig. 50, p. 62. If we compare curves *A*, *C*, and *D*, all corresponding to the same excitation, it is clear that exposure to the longer waves *before excitation* exerts a very marked influence upon the rate at which the phosphorescence, excited after this exposure, will decay. While the semi-permanent change produced by excitation is partly lost as the result of prolonged rest in the dark, rest alone is not a very satisfactory means of restoring the substance to a standard condition. Thus a rest of 24 hours brings about a change in the decay curve following a 10-second excitation from *C* to *A*. Rest for several days would shift the curve somewhat farther to the left. But even a rest of several weeks failed to bring the decay curve as far to the left as curve *D*.

Curve *D*, Fig. 50, was taken after an exposure of 4 minutes to the longer waves. A very much shorter exposure would have been nearly, if not quite, as effective. This point is brought out by the curves of Fig. 63, which were taken to determine the way in which the effect depended upon the duration of exposure to the longer waves. In taking these curves the procedure was as follows: In each case the screen was first exposed for 2 minutes to the mercury arc; the phosphorescence was then allowed to decay for 2 minutes, at the end of which time, while still visible, it was too faint for measurement. The screen was then exposed to the rays of a 50 c.p. lamp at a distance of 5 inches, a piece of ruby glass being interposed between the lamp and the screen; the duration of this exposure was 1 second for curve *III*, 3 seconds for curve *IV*, and 60 seconds for curve *V*. After this exposure to the longer waves the screen was excited by the mercury arc for 10 seconds, and the decay curves shown in Fig. 63 were observed by the procedure described on page 58.

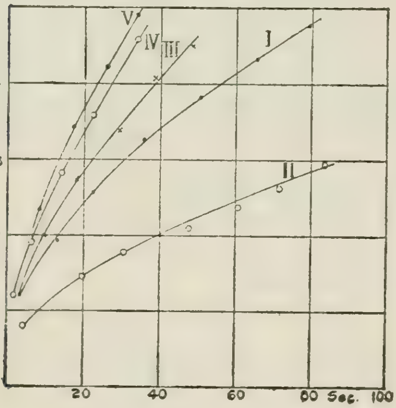

Fig. 63.

Effect on the decay curve of exposure to the infra-red for different times.

Curve *I*, 10 seconds exposure after 48 hours rest in the dark; *II*, 2 minutes exposure; *III*, 10 seconds exposure after 1 second infra-red; *IV*, 10 seconds exposure after 3 seconds infra-red; *V*, 10 seconds exposure after 60 seconds infra-red.

It will be observed that even an exposure of only 1 second is more effective than 48 hours rest. It will be noticed also that 3 seconds exposure to the longer waves is nearly as effective as an exposure of a minute.

With red and infra-red rays of less intensity a longer time is required to destroy the effect of previous excitation. The curves of Fig. 64 were taken with a procedure similar to that for Fig. 63, except that the distance of the 50 c.p. lamp from the Sidot blende screen was 30 inches instead of 5 inches. Exposure for 60 seconds to these less intense rays produces as great an effect as a similar exposure to the stronger rays. But this is not true for shorter exposures. While the ultimate effect of the weaker rays is apparently the same, more time is required to produce the change when the rays are of small intensity; approximately, at least, the change produced depends upon the product of intensity and duration of exposure.

The experimental data bearing upon this phase of the subject are so meager as to permit of only the most general conclusions, and additional experiments are much to be desired. So far as they go, however, the results indicate that the condition in which the material is left after the excitation and decay of phosphorescence is an unstable one, due perhaps to some new grouping of the molecules of the phosphorescent material. During rest in the dark accidental disturbances of various kinds may cause the substance to return more or less completely to its normal condition. The effect of rest is therefore uncertain, depending as it does upon the extent to which various obscure and perhaps unrecognized agencies are active; but certain waves lying chiefly in the infra-red region of the spectrum have a definite and positive effect in restoring the substance to its normal condition.

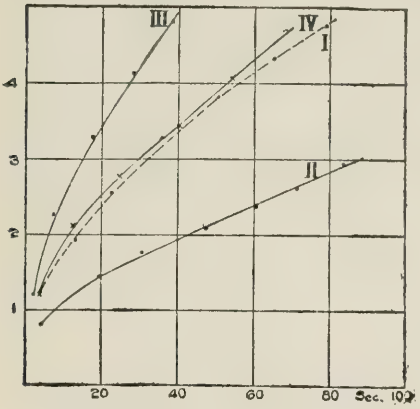

Fig. 64.

Effect on the decay curve of exposure to the infra-red for different times. The intensity of the infra-red rays was here only about $\frac{1}{36}$ of the intensity used for the curves of Fig. 63.

Curve *I*, 10 seconds exposure after 48 hours rest in the dark; *II*, 2 minutes exposure; *III*, 10 seconds exposure after 60 seconds infra-red; *IV*, 10 seconds exposure after 15 seconds infra-red.

INFLUENCE OF THE LONGER WAVES DURING EXCITATION.

We have seen that a condition is developed in Sidot blende by excitation which is favorable to the production of strong luminescence by a subsequent excitation. A long excitation is therefore more effective than exposure to equally intense exciting rays for a shorter period; for the favorable condition developed in the early stages of excitation makes the exciting rays that act later more effective. The luminescence of such a substance during excitation—*i. e.*, the fluorescence—will be relatively weak when excitation first begins and will increase in intensity as the exposure continues, reaching a steady value only after a considerable time. In Sidot blende, with the exciting light used in most of our experiments, 3 or 4 minutes were required to reach a steady value.[1]

The steady condition finally reached is manifestly characterized by equality in the rates of development and decay of the condition favorable to luminescence to which we have just referred. If we think of this favor-

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[1] See the preceding chapter of this memoir.

able condition as being due to some new grouping of the molecules, then the condition of steady fluorescence is reached when these favorable groups are being broken up, either spontaneously or through the action of some outside agent, just as rapidly as they are formed by the action of the exciting light.

It is clear that the intensity of steady fluorescence will be made less by any agent which increases the rate at which the assumed favorable grouping is destroyed. Now it is precisely this effect that is exerted by the red and infra-red rays; and we should therefore anticipate that the fluorescence of Sidot blende would be diminished by the action of longer rays.

This effect of the longer waves, which does not appear to have attracted much attention heretofore, may readily be made very marked indeed. Thus the rays from a projecting lantern after passing through a sheet of hard rubber 0.2 mm. thick are able to reduce the fluorescence of Sidot blende so greatly as to leave the intensity only a few per cent of its normal value, and this too with very intense excitation. If the ultra-violet rays of a spark are used for excitation numerous lecture experiments may be devised for demonstrating the existence of the invisible rays at the two ends of the spectrum. As compared with the experiments first proposed by Dahms,[1] in which the effect of the infra-red rays upon phosphorescence is utilized, this procedure has the advantage of giving a persistent rather than a fleeting effect.

In studying the influence of the longer rays upon fluorescence we have directed our attention especially to the distribution of the effect throughout the fluorescence spectrum. While the result of exposure to longer waves is to diminish greatly the *total* brightness of the fluorescence light, it might be that in certain restricted regions of the spectrum the intensity would be increased rather than diminished, or at least that the effect of the infra-red rays would vary greatly in magnitude in different parts of the fluorescence spectrum.

For the study of this phase of the subject the Sidot blende screen was mounted in front of a Lummer-Brodhun spectrophotometer, with an acetylene flame as a comparison source as in our previous work. The infra-red rays from an arc fell upon the screen after passing through hard rubber. The intensity of fluorescence was then measured in different parts of the spectrum, first with and then without the action of the longer waves, the excitation remaining constant. As exciting source a mercury-vapor lamp was first used, the lamp being made of the so-called "Uviol" glass, which possesses an unusual transparency to the ultra-violet rays.

In Fig. 65, curve *I*, shows the ordinary fluorescence spectrum of Sidot blende produced by the mercury lamp, while curve *II* shows the spectrum as modified by exposure to the infra-red. In the case of curves *I'* and *II'* a sheet of ordinary glass was interposed between the lamp and the screen, so that the ultra-violet rays were in large part removed from the exciting light. It is clear that the ultra-violet rays of the Uviol lamp introduce a band at about 0.49 μ which overlaps and distorts the usual green band at 0.51 μ.

A more annoying source of disturbance in these experiments, however, was the light reflected from the screen, which was mixed with fluorescence

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[1] Dahms, *l. c.*

light and practically inseparable from it. By making observations only at points lying between the bright lines of the mercury spectrum we had expected to be untroubled by reflected light. But owing either to optical imperfections in the apparatus or to the existence of a faint continuous spectrum in the light from the lamp, there was always enough reflected light in the field of the spectrophotometer to be an important and disturbing factor. To get some idea of the intensity and distribution of this reflected light we made the observations plotted as curve *R* in Fig. 65 with a screen of MgO on cardboard instead of the Sidot blende screen. To avoid confusion this curve is displaced downward in the plot. The intensity for points on curve *R* should be read from the right-hand side of the figure.

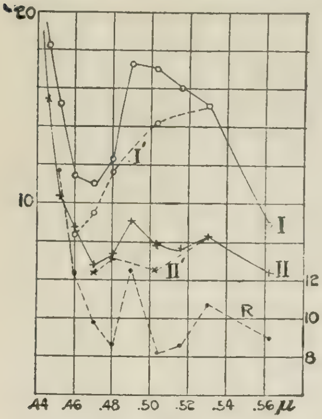

Fig. 65.

Effect of infra-red on fluorescence. Sidot blende excited by "Uviol" mercury-vapor lamp.

Curve *I*. Fluorescence spectrum.
Curve *II*. Fluorescence spectrum when screen is exposed to infra-red during excitation.
Curve *I′*. Fluorescence spectrum with plate glass between screen and mercury lamp.
Curve *II′*. Same as *I′*, except that screen is also exposed to infra-red.
R. Reflection of exciting light from white surface.

The irregular distribution of the reflected light and the great uncertainty in its measurement make the experiments plotted in Fig. 65 of little quantitative value. Especially is this true for the violet end of the spectrum, where the reflected rays are of great intensity. We could not even feel sure that the longer waves produced any effect at all in this region.

With a different zinc sulphide screen, the so-called "Emanations-pulver" referred to in Chapter IV, the conditions were somewhat more favorable. The curves in Fig. 66 show the ordinary fluorescence spectrum (curve *I*); the fluorescence spectrum with exposure to weak infra-red rays (curve *II*); the fluorescence spectrum during exposure to strong infra-red rays (curve *III*); and the reflected light determined as before. Different intensities of infra-red were obtained by using in one case one piece of black rubber and in the other case two pieces between the arc lamp and the screen. By this procedure it is possible to

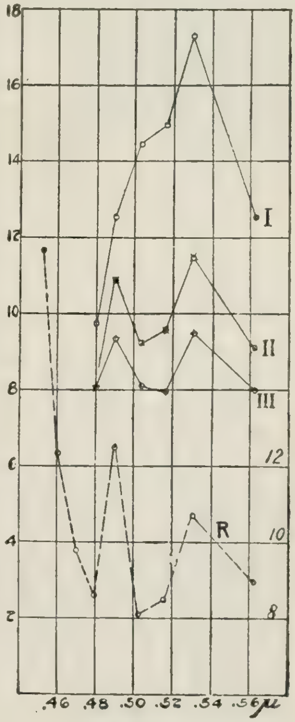

Fig. 66.

Effect of infra-red on fluorescence of "Emanations-pulver," excited by Uviol lamp.

determine the *ratio* of the effects produced by strong and weak infra-red, in spite of the uncertainty in the value of the reflected light. Thus the difference between the ordinate of curve *I* and the corresponding ordinate of curve *II* is a measure of the effect produced by weak infra-red; reflected light, since it affects both measurements, is eliminated by taking their difference. Similarly the difference between the ordinates of curves *I* and *III* measures the effect of the stronger infra-red. It is interesting to note that the ratio of these effects is nearly constant throughout the green band. Beginning at 0.562 μ and running toward the violet the ratio has the values: 1.32, 1.36, 1.31, 1.22, 1.94. Except for the last point, which is so near the edge of the band that the intensity of fluorescence is small, the values are constant to within observational errors. This fact adds another to the many that have been observed in the course of our work on luminescence to indicate that each band in a luminescence spectrum behaves as a unit—that whatever affects one part of the band affects all other parts of the band in the same proportion.

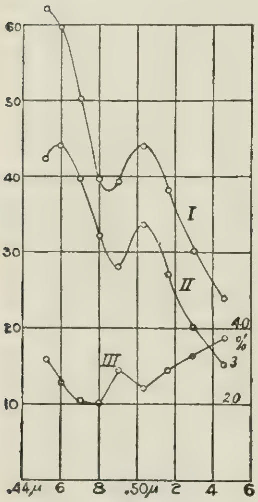

Fig. 67.

Effect of infra-red upon fluorescence of "Emanations-pulver" excited by ultra-violet rays of an iron spark.

A more satisfactory method of studying the effect in question is to use only ultra-violet light in excitation. All troubles due to reflected light are in this case removed. The results of this procedure in the case of the original Sidot blende used in our earlier experiments are shown in Fig. 67. An iron spark was used as an exciting source, a spectrum being formed by a quartz train and only the ultra-violet rays used. The source of infra-red was an arc lantern whose rays passed through a sheet of hard rubber 0.2 mm. thick. The effect of exposure to longer rays during excitation by the ultra-violet rays of the iron spark was to change the fluorescence from curve *I* to curve *II*. The diminution in intensity brought about by exposure to the longer rays, expressed as a fraction of the ordinary fluorescence at the same wave-length, is given in curve *III*.

More extended experiments are required to determine whether the change in the effect from 38 per cent at 0.546 μ to 20 per cent at 0.480 μ is real or the result of errors. It does not seem likely, however, that experimental errors alone can account for so great a change. In interpreting the results we must bear in mind the fact that the spectrum shown in Fig. 67 obviously consists of two overlapping bands, and that the infra-red effect may differ for the two. It is highly probable also that still another band is present at 0.49 μ, as was found to be the case with ultra-violet excitation in the experiments plotted in Fig. 65; and for this band the effect of the longer waves may be different still. It is clear that further experiments on this branch of the subject are needed.

EFFECT OF THE LONGER WAVES DURING DECAY.

In studying the effect of the infra-red rays upon the decay of phosphorescence two methods were used. In the first of these the intensity of the total phosphorescent light was measured by a photometer at different times after excitation had ceased, as described in Chapter IV. The violet end of the carbon arc spectrum was used for excitation, and a 50 c.p. incandescent lamp as a source of infra-red rays. In these experiments a cell containing a solution of iodine in carbon disulphide was used instead of hard rubber to remove the visible rays. The distance of the lamp from the Sidot blende screen was about 60 cm.

The curves of Figs. 68 and 69 show some of the results obtained by this procedure. In Fig. 68, curve *I* is the ordinary decay curve without exposure to infra-red. In the case of curve *III* the infra-red rays were allowed to fall on the screen when the decay had proceeded for about 32 seconds. In curve *II* the infra-red rays were turned on about 4 seconds after the end of excitation and were cut off again at the end of about 19 seconds. The great increase in the rapidity of decay brought about by infra-red rays, even when of such small intensity as those used in these experiments, is clearly shown.

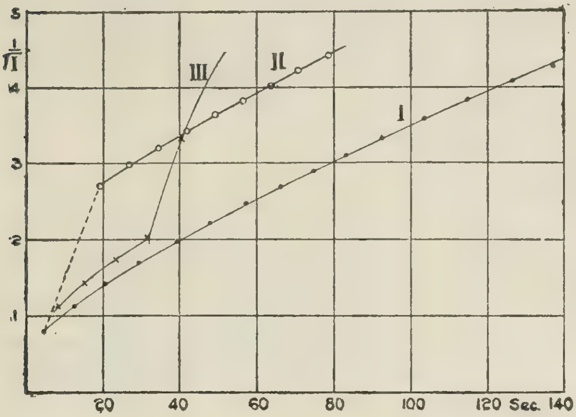

Fig. 68.

Influence of exposure to infra-red during decay upon the form of the decay curve.

Curve *I*. Ordinary decay curve.
Curve *II*. Screen exposed to infra-red after decay had proceeded for 4 seconds. Infra-red cut off at $t=19$ seconds.
Curve *III*. Screen exposed to infra-red after decay had proceeded for 32 seconds.

There was no indication in these experiments of any temporary *increase* in the brightness of phosphorescence when the rays were first turned on, as has been noted by many observers in the case of Balmain's paint and other phosphorescent sulphides. Dahms has already called attention to this peculiarity of Sidot blende. The effect of the longer waves in suppressing phosphorescence has sometimes been explained by assuming that these rays act in the same way as does a rise of temperature; *i. e.*, that they accelerate the process which causes phosphorescence, so as to produce a brief flash, due to the sudden liberation of the energy stored during excitation, followed by a complete loss of luminescence when the stored energy has been used up. While this explanation of the phenomenon may be correct for the other phosphorescent substances it can not be applied without essential modification to the case of Sidot blende. It has recently been shown, however, by Ives and Luckiesh[1] that under some circumstances a

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[1] Physical Review, xxxii, p. 240, 1911. The specimen of Sidot blende that was tested by Ives and Luckiesh differed from that used by us and other observers in the fact that the law of decay after one minute was $I^{-0\cdot97}=a+bt$ instead of $I^{-\frac{1}{2}}=a+bt$. It thus forms the only exception known to us to the law of decay discussed in Chapter XV.

flash may be observed immediately after exposure to infra-red rays even in the case of Sidot blende. These observers find that "there are two stages in the decay of phosphorescence, merging gradually one into the other. In the first stage the effect of long waves is to cause a sudden drop in intensity; in the second stage the long waves cause a temporary increase of brightness before decay. In the intermediate stage the accelerated decay appears to the unaided eye to be delayed in starting." With intense infra-red rays the preliminary flash could be made to occur as early as 30 seconds after the end of excitation.

Perhaps the most striking feature of the curves in Fig. 68 is the nearly exact parallelism that exists between the later part of curve *III* (after the infra-red rays were cut off) and the straight part of the ordinary decay curve. The action of the longer waves appears to be to bring the material quickly into the same condition as regards ability to emit light that it would have acquired at the end of a much longer period of ordinary decay. The results of Ives and Luckiesh are not in accord with this view.

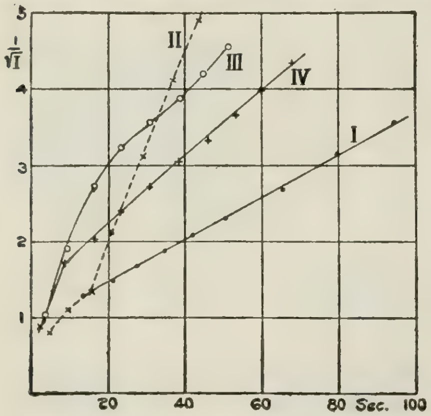

Fig. 69.

Influence of exposure to infra-red during decay upon the form of the decay curve.

Curve *I*. Ordinary decay curve.
Curve *II*. Screen exposed to infra-red after the decay had proceeded for 18 seconds.
Curve *III*. Screen exposed to infra-red during excitation and for first 16 seconds of decay.
Curve *IV*. Screen exposed to infra-red during excitation and for first 9 seconds of decay.

In the brief abstract of their work referred to on page 77 they state that "the decay curve after brief action of red or infra-red does not correspond with the original curve with origin shifted."

In the case of curves *III* and *IV* of Fig. 69 the screen was exposed to infra-red during excitation and during the early stages of decay. The infra-red rays were cut off at the points indicated by the break in the curves. It will be noticed that the latter portion of curve *III* is nearly parallel to the straight part of the ordinary decay curve; but in curve *IV*, where the infra-red was cut off earlier, the straight part of the curve is not even approximately parallel to curve *I*. The results shown in Fig. 69 are thus in agreement with the statement of Ives and Luckiesh.

For the early stages of decay a number of curves were taken by means of the spectrophotometer, the method being that described in Chapter III. With this method it is impracticable to follow the decay for more than a few seconds, since the illumination of the spectrophotometer field soon becomes too faint for accurate measurements. The method possesses a great advantage, however, in the fact that the effect of the long waves can be determined for different parts of the phosphorescence spectrum.

For the curve shown in Figs. 70 and 71 the exciting light was the violet of the carbon arc spectrum. For the curves of Figs. 72 to 75 a spark between cadmium terminals was used in excitation. The intensity of phosphorescence has been plotted in all of these curves instead of the reciprocal square root, although in some cases the latter value has been plotted also.

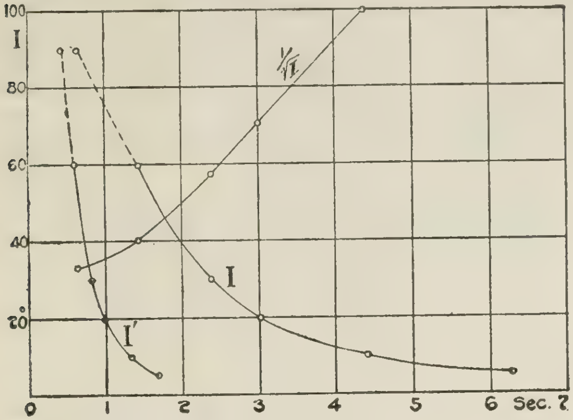

Fig. 70.

Influence of exposure to infra-red on form of decay curve.

Curve *I*. Ordinary decay curve for λ = 0.497 μ.

Curve *I'*. Screen exposed to infra-red immediately after end of excitation.

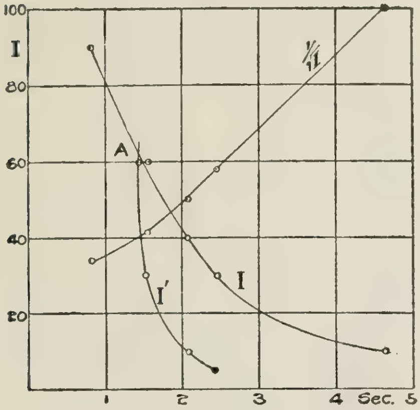

Fig. 71.

Curve *I*. Ordinary decay curve for λ = 0.497 μ.

Curve *I'*. Screen exposed to infra-red after decay had proceeded to *A*.

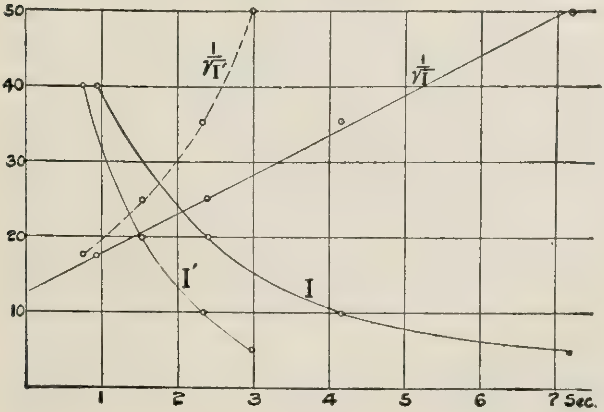

Fig. 72.

Decay curves with and without infra-red. λ = 0.5460.

In all these figures the curve marked I was taken without infra-red[1] and that marked I' with infra-red. In general the exposure to infra-red began at the instant the excitation ceased, the shutter being arranged so that the same movement that cut off the exciting rays allowed the infra-red rays to fall upon the screen. In the case of Fig. 71 exposure to the infra-red did not begin until about 1.4 seconds after the end of excitation. Numerous curves of this kind were taken in which the exposure to infra-red began at different times after the beginning of decay. All of these curves show the same sudden drop in intensity at the instant that the long waves begin to act.

The curves of Figs. 70, 71, and 72, except for the method of plotting, are quite similar to the curves for the total light obtained by the photometer method first described. Apparently the action of the longer waves during the first few seconds of decay is quite similar to its action later. It will be observed that the curves of Figs. 70 to 72 refer to regions of the phosphorescence spectrum either near the maximum or toward the red edge of the band.

Figs. 73, 74, and 75 show the influence of the longer waves upon those regions of the fluorescence spectrum lying near and beyond the violet edge of the green band. Here the effect seems to be entirely different. At 0.445 μ (Fig. 75) the effect of exposure to infra-red is to retard the decay of phosphorescence instead of to accelerate it. In the region lying between the green band (0.51 μ) and the violet band (0.45 μ) the effect of the infra-red is at first to retard the decay and later to accelerate it (Figs. 73 and 74).

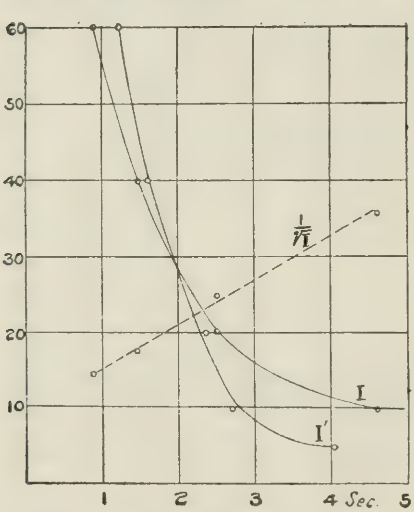

Fig. 73.

Decay curves with and without infra-red. $\lambda = 0.474\ \mu$.

Owing to the faintness of the spectrophotometer field and the rapidity with which the phosphorescence decays it is difficult to determine the form of the curves in the early stages of decay with accuracy. Especially is this true in the blue and violet, owing to the small luminosity of this region of the spectrum. Each point plotted represents, however, the average of a number of separate readings. For each pair of points the observations for the time of decay with and without infra-red were taken alternately. No special precautions were taken to keep the exciting source constant. The slight initial curvature of the line $I^{-\frac{1}{2}}$ in Figs. 70 and 73, where the exciting light was from the carbon arc, is perhaps to be explained as the result of variations in this source. In the case of the other observations, in which a spark was used in excitation, the points for $I^{-\frac{1}{2}}$ lie reasonably well

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[1] The carbon arc was used as a source of infra-red, a piece of dense ruby glass serving as a filter. Red light, and perhaps a little yellow light, was therefore present in addition to the infra-red. There has been nothing in our experiments to indicate that the presence of these visible rays modifies the results in any way.

upon a straight line, and thus give a check upon the accuracy of the observations.

The remarkable reversal in the effect of infra-red in passing through the luminescence spectrum received ample qualitative confirmation. With the spectrophotometer set for some region in the blue or violet the brightness of the field increased noticeably for a few seconds when the screen was exposed to infra-red during decay, even when the exposure first began several seconds after the end of excitation. The same effect was observed in the case of "Emanations-pulver" and Balmain's paint. In the case of the latter substance the flash that accompanied exposure to the longer waves developed more slowly and lasted longer than in the case of Sidot blende.

Two interpretations of the results brought out in Figs. 70 to 75 suggest themselves. Neither, however, is wholly satisfactory.

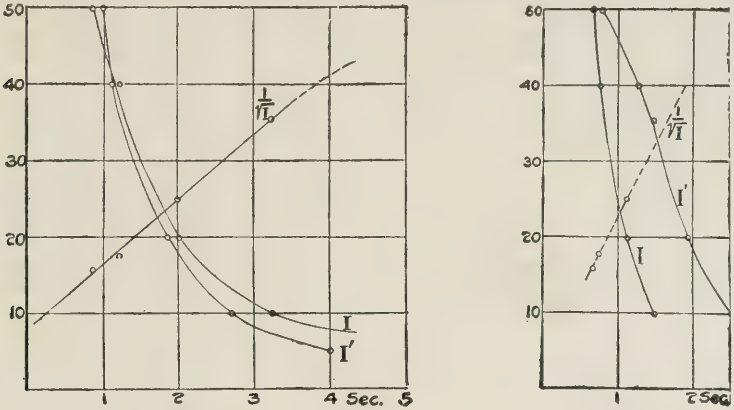

Fig. 74.

Fig. 75.

Decay curves with and without infra-red. λ = 0.464 μ (Fig. 74) and λ = 0.445 μ (Fig. 75).

In all of these experiments the luminescence spectrum consisted of two bands, namely, the green band at 0.51 μ and the violet band at about 0.45 μ. It is possible that the infra-red rays retard the decay of phosphorescence in the case of the violet band and accelerate it in the case of the green band. In the curves of Fig. 75 we are dealing with the violet band only; in Figs. 70, 71, 72, and 74 the light is almost entirely from the green band; but at wave-lengths 0.474 μ (Fig. 73) and 0.464 μ (Fig. 74) the light entering the collimator slit comes partly from one of these bands and partly from the other. The violet band apparently decays more rapidly than the green band. (Compare the slant of the line for $I^{-\frac{1}{2}}$ in Fig. 75 and Fig. 72.) If the violet band is initially the brighter of the two the retarding effect of the infra-red upon the decay of this band will predominate in the early stages of decay. Later, when the violet band has nearly died out and the light is chiefly due to the green band, the opposite effect will predominate. The two curves I and I' will therefore intersect, as shown in Fig. 72 and Fig. 74.

Two objections may be urged to this explanation. If the light in the case of Figs. 73 and 74 is from two bands that decay at different rates we should hardly expect the relation between t and $I^{-\frac{1}{2}}$ to be as simple as the linear relation that holds for the green band alone. Yet the deviation from a linear relation in both these cases is well within the errors of observation. Again, if the infra-red rays increase the brightness of the violet band after excitation has ceased it would seem reasonable to expect a similar effect during excitation. Yet the effect during excitation (Fig. 67) is nearly the same for both bands.

We were first led to expect increased brightness in the violet during exposure to the infra-red, and to undertake experiments in the hope of detecting such an effect, as the result of an entirely different line of reasoning. Looking upon phosphorescence as due to the recombination of ions dissociated by the action of the exciting light, we may explain the fact that the phosphorescence light is of greater wave-length than the exciting light (Stokes's law) briefly as follows: Dissociation results from the violent resonant vibration of a neutral molecule of the active substance under the influence of the exciting waves. The wave-length of maximum resonance and therefore maximum excitation is determined by the natural period of vibration of the active molecule, which is influenced to some extent, but not greatly, by the surrounding solvent. The charged ions resulting from excitation will, however, be attracted by the neutral molecules of the solvent and will form the nuclei of heavy aggregations of molecules; and recombinations of the ions will therefore occur under conditions which make the resulting vibrations longer, on the whole, than the period of the active molecules before dissociation; hence the well-known displacement of the luminescence spectrum with reference to the absorption spectrum.

Now the effect of the infra-red rays may be to so shake up the molecules of the solvent as to prevent the loading down of the ions by the attraction of neutral molecules, or to destroy such heavy aggregations if already formed. Under the influence of the infra-red, therefore, the light emitted will be due largely to the vibrations that occur during the recombination of unloaded ions and will be of the same wave-length as that which the active substance absorbs. If the screen is exposed to infra-red rays after excitation we should expect a decrease in the intensity of phosphorescence throughout the phosphorescence band due to the breaking down of the groups of molecules referred to above. But owing to the resulting increase in the number of unloaded ions we should also expect the emission of light whose wave-length is that of the resonant absorption band of the substance. Now the absorption band always lies on the ultra side of the luminescence band, and usually the two bands overlap. (That this is the case with Sidot blende is shown by the fact that this is one of the substances for which Stokes's law, in its strict form, is violated.) Exposure to infra-red should therefore produce increased intensity near and beyond the violet edge of the phosphorescence band; which is exactly what we have observed.

In the region where the absorption and emission spectra overlap, the effect will be more complicated. While the light in this region due to the ordinary luminescence band will diminish, there will be at the same time a temporarily increased emission due to the recombination of the unloaded ions that are shaken loose by the infra-red vibrations. A bright flash immediately after the exposure to infra-red, followed by decay more rapid than the normal, is therefore to be expected in the intermediate region corresponding to Figs. 73 and 74.

The effect of the longer waves during excitation is unfortunately as hard to reconcile with this explanation of the phenomena as with that first suggested.

VARIATIONS OF THE EFFECT WITH THE LENGTH OF THE LONGER WAVES.

In the case of several phosphorescent substances, including Sidot blende, the effect of rays of different wave-length in suppressing phosphorescence has been studied photographically by Dahms.[1] Our own results, obtained by an entirely different method, in general confirm his conclusions in a very satisfactory way.

The arrangement of apparatus was similar to that used in our first experiments on the decay of phosphorescence.[2] A spark was used for excitation and a shutter was so arranged that the screen was exposed to the infra-red rays and the phosphorescent light allowed to fall on the slit of the spectrophotometer at the same instant that the excitation was brought to a close by short-circuiting the spark. A Nernst glower was used as a source of infra-red rays. This was mounted in the place of the slit of a large mirror spectrometer having a quartz prism.[3] The Sidot-blende screen was covered with black paper except for a narrow rectangular region having about the same width as the Nernst glower. The adjustment of the spectrometer having been determined by observations in the visible spectrum, wave-lengths in the infra-red were computed from the angle of deviation. The effect of different rays from the Nernst glower was measured by the difference between the times required for the phosphorescence to fall from its initial intensity to a definite final intensity with and without exposure to the rays to be tested. Each point of the curves shown in Fig. 76 is determined from the average of ten observations with infra-red and ten without, the observations being made alternately. The difference between the two, expressed as a fraction of the normal time of decay, has been plotted for the different wave-lengths used, which ranged from 0.6 μ to 2.3 μ. The observations refer to the region of maximum intensity in the phosphorescence spectrum (0.512 μ).

Referring to Fig. 76, it will be seen that the effect of the longer waves is observable to some extent in the visible region. A maximum is reached at about 0.9 μ, followed by a minimum at about 1.0 μ and another maximum at 1.3 μ. From 1.2 μ on the observations were repeated under slightly different conditions the following day (see broken line). In this case the chief maximum appears to lie at 1.37 μ. The results are probably in all cases uncertain to the extent of 2 or 3 per cent, and errors are especially likely to be serious in regions where the effect is small. For this reason we can not feel certain of the third maximum at 2.18 μ, although the probability is that it really exists. As far as any important effect is concerned, however, our results confirm the conclusion of Dahms that the action does not extend beyond 1.5 μ.

It can scarcely be doubted that absorption of the active rays is necessary before they can produce any effect upon phosphorescence. It seems

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[1] Dahms; Annalen der Physik, 13, p. 425.

[2] See Chapter III of this memoir.

[3] Tests (by direct eye observation) with a rock-salt prism showed that no effect was observable for wave-lengths longer than those transmitted by quartz.

probable, therefore, that Sidot blende possesses broad absorption bands with maxima not far from 0.9 μ and 1.35 μ. Experiments with other phosphorescent substances having ZnS as their base will be necessary to determine whether the absorption that determines this effect on phosphorescence is characteristic of the solvent (ZnS) or of the dissolved metal causing luminescence. It is interesting to note, however, that in the absorption spectrum of sphalerite (ZnS) Coblentz has found evidence of bands at about 0.9 μ and 1.4 μ. While Coblentz's work does not indicate great absorption at these points, it must be remembered that they fall in the most intense region of the spectrum of a Nernst glower, so that the total amount of energy absorbed might be very considerable.

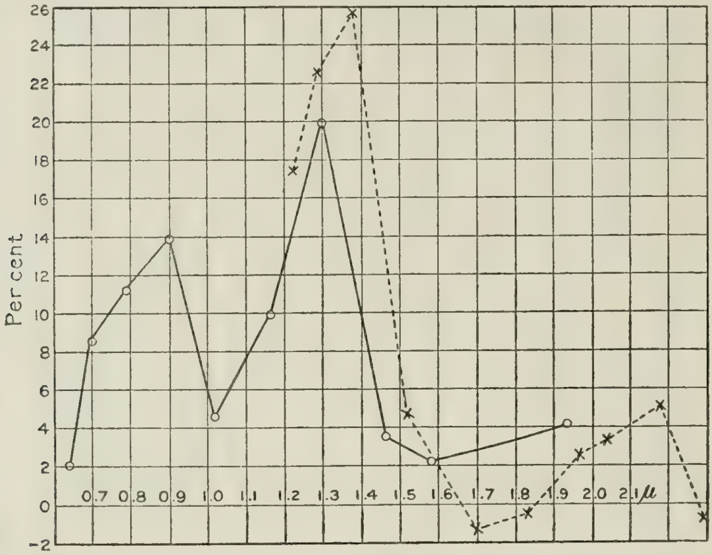

Fig. 76.

Effect of infra-red rays of different wave-length. Ordinates represent the percentage diminution in the time of decay under the influence of infra-red.

CHAPTER VI.

VARIATIONS IN THE DECAY OF PHOSPHORESCENCE PRODUCED BY HEATING.

In connection with the investigations described in Chapters IV and V Dr. C. A. Pierce, during the years 1906–1908, made an extended study of the phosphorescence of Sidot blende and of Balmain's paint at temperatures ranging from room temperature to 300° C. The present chapter contains a summary of his results.[1]

EXPERIMENTS WITH SIDOT BLENDE.

The apparatus used was similar in principle to that described in Chapter IV, p. 58, but was modified to adapt it to the conditions of the experiment. The substance studied was the phosphorescent zinc sulphide already referred to as "Emanations-pulver." It was placed in a shallow dish and heated by means of an electric furnace capable of being readily removed and replaced in its position relative to the powder without disturbing the latter.

The temperature of the powder was measured by means of a thermo-junction embedded in the mass. Phosphorescence was excited by a mercury-arc lamp of the Lummer type.

By means of properly placed mirrors the exciting light was reflected upon the surface of the powder and the phosphorescent light was reflected through a double window of mica and plate glass into the field of a Lummer-Brodhun photometer. The adjustments were such that the conditions of illumination and observation were the same whether the powder was within the furnace or outside. The comparison light was an acetylene flame with diaphragm. A color match was obtained by the interposition of colored glasses and the balance of illumination in the field of the photometer by moving the comparison light.

The apparatus was arranged so that a single observer, working in a dark room, could automatically record all observations such as the times of opening and closing the shutter of the exciting lamp, the beginning and end of heating, the times at which photometric observations were made, and the position of the comparison light on the photometer bar. The observer could likewise make all manipulations during a complete run without taking his eye from the observing telescope. Before each set of observations the powder was exposed to infra-red rays for 1 minute and allowed to remain in darkness for 5 minutes before excitation in order, as already described in Chapter IV, to secure a standard condition. In the present case the action of the infra-red was not sufficient to destroy all thermo-luminescence when the powder was heated to 350° C., but the effect was so reduced that even after the strongest previous excitation the thermo-luminescence could not be measured with the photometer. The infra-red rays, which

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[1] C. A. Pierce, Physical Review, XXVI, pp. 312 and 454.

were from a 16 c.p. incandescent lamp with a screen of thin vulcanite, heated the powder slightly, but the wait of 5 minutes allowed it to cool to approximately room temperature.

The effect of temperature upon the decay curve, when the Sidot blende is excited and allowed to decay at the same temperature, is shown in Fig. 77.

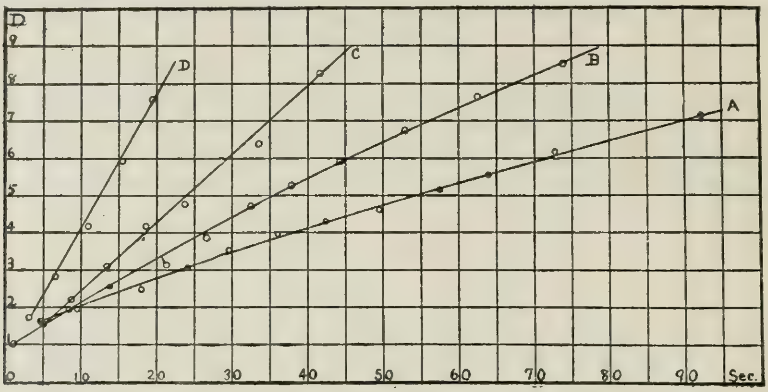

Fig. 77.

Effect of temperature during excitation and decay. Excited 40 seconds. Curve *A*, temperature 21° C.; curve *B*, temperature 37° C.; curve *C*, temperature 60° C.; curve *D*, temperature 85° C.

The curves are plotted with distances of the standard lamp from the photometer screen as ordinates and time reckoned from the end of excitation as abscissas. The ordinates are therefore inversely proportional to the square roots of the intensities. Curves *A* and *B* are concave downward throughout, while *C* and *D* are approximately straight lines. In fact, the points on curve *D* indicate an upward bending. The initial intensity evidently increases and the decay becomes more rapid as the temperature is raised.

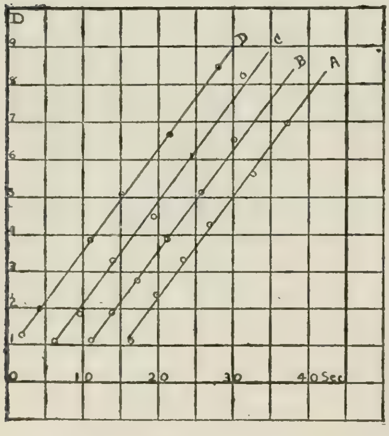

Fig. 78.

Effect of temperature during excitation and decay. Excited 400 seconds. Temperature 93° C.

To further test the form of the curve of decay at high temperatures, a series of runs was made with constant length of excitation and constant temperature. Four runs of the series are shown in Fig. 78. If the curves had been plotted with the actual times as abscissas, they would coincide. In order that the eye may be able to distinguish readily the points on each curve, the four curves are separated by plotting curve *D* with the abscissas marked on the figure and displacing the remaining curves each 5 seconds farther to the right. It is evident that the curves are straight lines throughout the time of observation, but it is probable that they would show a downward bending nearer the origin. Studies of curves of very rapid decay, to be described in Chapter VII, greatly strengthen this view. The conclusion that at room temperature the observed part of the decay curve is concave downward and becomes less concave as the temperature is raised is substantiated by several series of curves which are not reproduced.

A possible explanation of the changes in the decay curve that occur when Sidot blende is excited at different temperatures may be deduced as follows: Let it be assumed that the law of decay for a single band in the spectrum is[1]

$$I=\frac{1}{(a+bt)^2}$$

Let it be assumed that the phosphorescent spectrum of Sidot blende consists of two bands, and let curves *AB* and *CD*, Fig. 79, represents the decay of these bands. The decay of the total intensity can be computed by the equation[2]

$$D=I^{-\frac{1}{2}}=\left[\Sigma\frac{1}{(a+bt)^2}\right]^{-\frac{1}{2}}$$

and is represented in Fig. 79 by the curve *OP*. This curve is concave downward throughout but approaches a straight line with increase in time. From Figs. 77 and 78 it can be seen that the effect of a higher temperature is to hurry the decay. Hence the slope of the lines representing the decay of the separate bands[3] will be greater at a higher temperature. *MN*, Fig. 79, represents the decay of the total intensity at the higher temperature. *M N* is concave downward throughout, but if the portion occurring within the first few seconds were not drawn, the remainder of the curve would

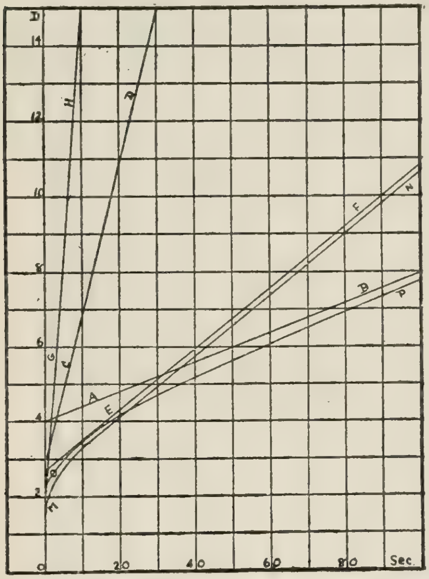

Fig. 79.

AB, decay of one band at a certain temperature; *CD*, decay of the other band at the same temperature; *OP*, decay of the total intensity due to the two bands; *EF*, decay of the first band at a higher temperature; *GH*, decay of the other band at the higher temperature; *MN*, decay of the total intensity at the higher temperature.

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[1] The law proposed by H. Becquerel. See Chapter XV.

[2] The law proposed by H. Becquerel for the decay of the total intensity when the phosphorescent spectrum consists of more than one band.

[3] The existence of two bands in the fluorescence spectrum of Sidot blende has been demonstrated in Chapter IV. The presence of two such bands in the case of the powder studied by Dr. Pierce was established by him by means of spectrophotometric measurements. Their maxima were found to be approximately at 0.53 μ and 0.41 μ. The same bands might therefore be expected in the phosphorescence spectrum.

appear to be a straight line, while under the same conditions the curve OP would still be seen to be concave downward.

The curves in Fig. 79 represent closely the facts deduced from Figs. 77 and 78. They also agree with the observations recorded in Chapter IV, which show that the decay curve consists of two straight lines gradually merging into one another. By changing the slopes and intercepts of the lines in Fig. 79 representing the decay of the single bands, a decay curve of the total intensity can be derived which will exactly fit the deductions mentioned above. Dr. Pierce's later experiments on the decay in Sidot blende (Chapter VIII) nevertheless make it seem very doubtful whether this explanation of the form of the decay curve, and of its dependence upon temperature, can be made to accord with all the experimental facts.

The effect of heating the Sidot blende after it has been excited at room temperature and allowed to decay at room temperature to a small fraction of its initial intensity of phosphorescence is illustrated in Figs. 80, 81, and 82. The result of this process is the well-known phenomenon of *thermo-luminescence.* The curves are plotted with intensities as ordinates and times, measured from the moment of heating, as abscissas. Higher temperatures increase the intensity of the outburst of light, and cause the maximum to occur sooner after the beginning of heating and to die away more rapidly.

In the case of Fig. 80 the initial intensity immediately after excitation was somewhat greater than $I=12$. The intensity was allowed to decay to $I=0.8$, when heating was begun. In the case of Fig. 82, the initial intensity was somewhat greater than $I=37$.

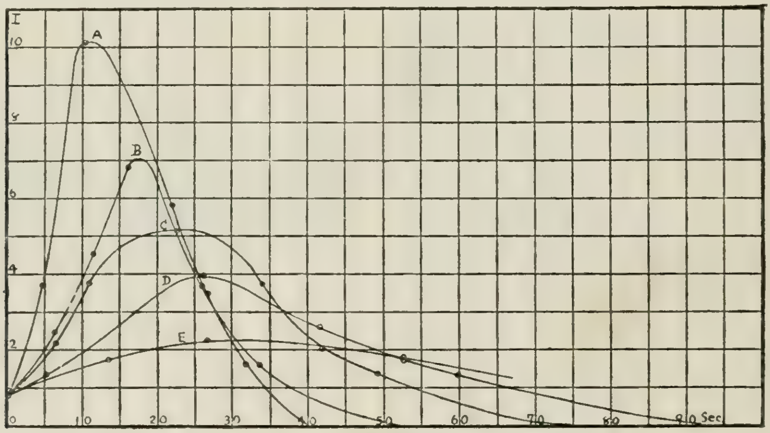

Fig. 80.

Effect of heating when the phosphorescence has decayed to an intensity equal to 0.8. Excited 10 seconds at room temperature. Curve *A*, heated to 307° C.; curve *B*, heated to 270° C.; curve *C*, heated to 208° C.; curve *D*, heated to 155° C.; curve *E*, heated to 99° C.

The effect of heating after excitation may be considered in one of two ways. Either it suddenly releases the energy represented by the phosphorescence, or else it sets up some new reactions in the powder. Though the decay had reached a low intensity before heating was begun in the runs shown in Figs. 80, 81, and 82, yet at this low intensity the decay was slow; hence there may have been considerable energy still left, which heating released to give the flash peculiar to thermo-luminescence. If this is the case, the areas between the curves in either Fig. 80, 81, or 82 and the coördinate axes should be equal to each other. It is impossible to get experimental data with which to draw the curves to the axis, so the author projected the curves tentatively. This is not an entirely rash thing to do, because a slight variation in the prolongations will have effect; furthermore, while the low intensities were not measurable, one could nevertheless get some idea of the rapidity of decay by noticing how rapidly the photometer screen became dark.

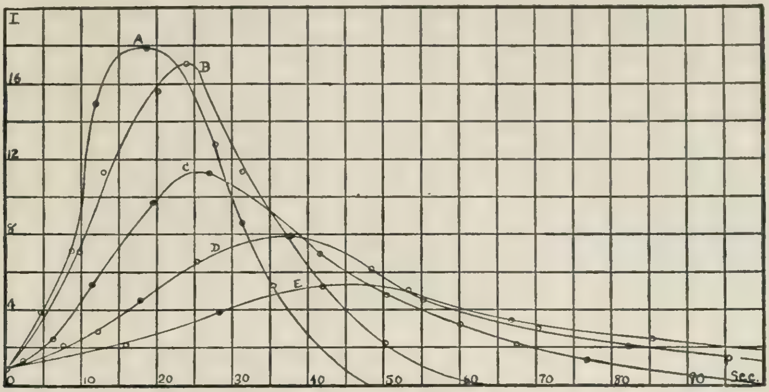

Fig. 81.

Curves similar to those in Fig. 81. Excited 80 seconds at room temperature. Curve *A*, heated to 308° C.; curve *B*, heated to 267° C.; curve *C*, heated to 206° C.; curve *D*, heated to 155.5° C.; curve *E*, heated to 99° C.

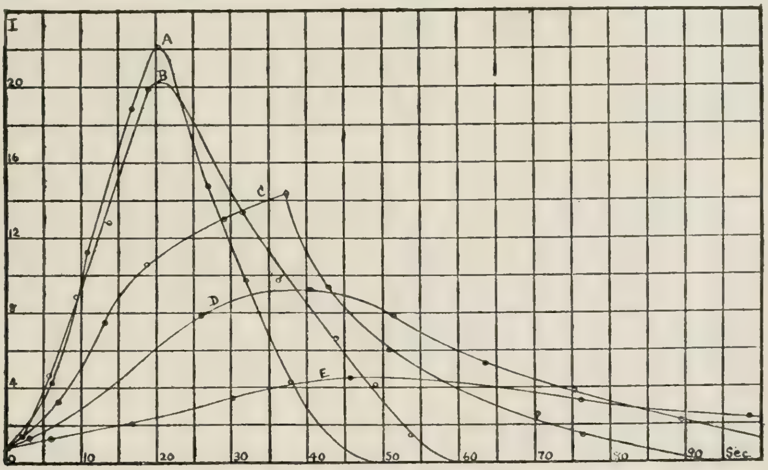

Fig. 82.

Curves similar to those in Figs. 80 and 81. Excited 320 seconds at room temperature. Curve *A*, heated to 309° C.; curve *B*, heated to 266° C.; curve *C*, heated to 207° C.; curve *D*, heated to 153° C.; curve *F*, heated to 98° C.

Fig. 83 shows the areas plotted with temperatures as abscissas.

If the areas had been equal to each other for a given excitation, each of the curves in Fig. 83 would have been a straight line parallel to the temperature axis. Aside from the low values at 300°, which are probably due to the approach to temperatures at which the substance loses its power to phosphoresce, the curves suggest by their approximation to horizontal lines that the function of heating is merely to release the stored energy more suddenly.

If this explanation of the effect of heating is correct, then it would be reasonable to expect that in the case of the curves of Fig. 77 the decay would be more rapid the higher the temperature, which effect has already been pointed out.

Fig. 84 shows the change in the maximum ordinate of the curves of thermo-luminescence as the temperature is raised. No weight is given to the exact shape of the curves, the points being connected merely to aid the eye in distinguishing them. The curves are in accordance with what would be expected if the function of the temperature is to liberate suddenly the phosphorescent energy. If this is the case, the greater the temperature the quicker the energy will be liberated and the brighter the flash. The relation of maximum intensity to temperature is shown more clearly in Fig. 85.

To ascertain the rapidity with which the powder within the furnace was heated, measurements were made for each of the temperatures at which curves of thermo-luminescence had been obtained, and from these curves were plotted showing the rise of temperature of powder and the variation in the temperature of the furnace. Fig. 86 gives the curves for two of these temperatures. The general conclusion from these measurements was that the powder reached a constant temperature in a constant time independent of the temperature. The periods of the two galvanometers used in the temperature measurements were too short to affect the shape of the curves appreciably.

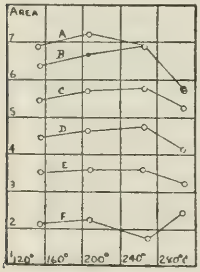

Fig. 83.

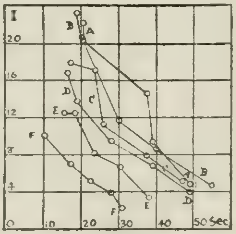

Fig. 84

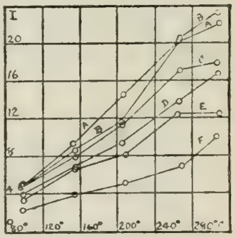

Fig. 85.

Fig. 83.—Areas between the thermo-phosphorescence curves and the coördinate axes. Curve *A*, excited 320 seconds (from Fig. 82); curve *B*, excited 160 seconds; curve *C*, excited 80 seconds (from Fig. 81); curve *D*, excited 40 seconds; curve *E*, excited 20 seconds; curve *F*, excited 10 seconds (from Fig. 80).

Fig. 84.—Change in the maximum intensity as the temperature is raised. Maximum intensity *vs.* time of maximum intensity measured from the beginning of heating. Curve *A*, excited 320 seconds (from Fig. 82); curve *B*, excited 160 seconds; curve *C*, excited 80 seconds (from Fig. 81); curve *D*, excited 40 seconds; curve *E*, excited 20 seconds; curve *F*, excited 10 seconds (from Fig. 80). Each point on a curve is for a given temperature. On each curve the lowest point is for 99° C. and for the other points in consecutive order 155°, 207°, 267°, and 308° C., respectively.

Fig. 85.—Increase of maximum intensity of thermo-luminescence with increase of temperature. Curve *A*, excited 320 seconds (from Fig. 82); curve *B*, excited 160 seconds; curve *C*, excited 80 seconds (from Fig. 81); curve *D*, excited 40 seconds; curve *E*, excited 20 seconds; curve *F*, excited 10 seconds (from Fig. 80).

The method of heating employed possesses several advantages. The temperatures are known and can be accurately reproduced as many times as desirable. Further, the gradual heating allows the flash to be followed in the photometer. For some other work a strip of platinum which supported a thin layer of the powder was heated by passing an electric current through the strip. The flash in this case occurred too rapidly to be followed, the maximum intensity being the only measurement possible.

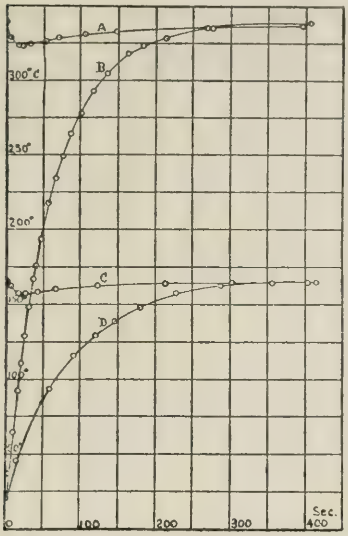

Fig. 86.

Curves *A* and *C*, variation in temperature of furnace when the powder is put in. Curves *B* and *D*, increase in temperature of the powder. Curves *A* and *B* do not become identical because they were not taken simultaneously and the temperature changed slightly between the two runs.

It is not easy to estimate the effect of gradual heating as compared with more nearly instantaneous heating. The outside layer of the powder is subjected to the temperature of the furnace, which does not vary widely. It is only the inside layers which are heated as slowly, as the curves in Fig. 86 indicate. It is not believed that any material change is introduced in the relation of the various curves, though the actual form of the curves may be changed more or less.

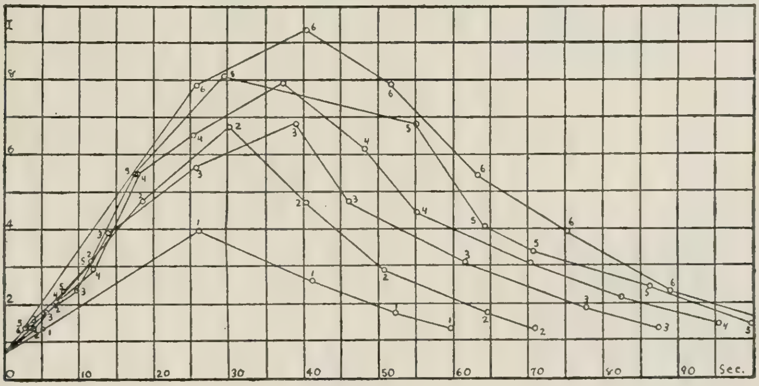

Fig. 87.

Effect of varying the length of excitation. Ordinates show the intensities of luminescence, and abscissas the times after heating began. The length of excitation and the temperature of the furnace are as follows:

Curve 6, 320 sec., 153.0° C.; curve 5, 160.0 sec., 155.5° C.; curve 4, 80.1 sec., 155.5° C.; curve 3, 40.0 sec., 155.5° C.; curve 2, 19.9 sec., 155.5° C.; curve 1, 10.0 sec., 155.0° C.

The effect of varying the length of excitation is brought out in Figs. 87 and 88. As in previous curves, the phosphorescence was excited at room temperature and allowed to decay to $I=0.8$ before heating. The points are joined by straight lines to aid the eye in following the individual curves. Two effects are noticeable at a glance. The maximum intensity increases with excitation and is shifted to the right, *i. e.*, comes at a later time. The effect of saturation is shown. This is brought out more clearly in Fig. 89.

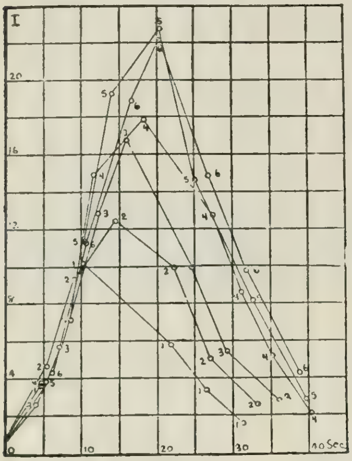

Fig. 88.

Fig. 88.—Curves similar to Fig. 87. Effect of varying the length of excitation. The length of excitation and the temperature of the furnace are as follows: Run 6, 320.1 sec., 309° C.; run 5, 159.9 sec., 308° C.; run 4, 80.2 sec., 308° C.; run 3, 39.9 sec., 308° C.; run 2, 20.0 sec., 309° C.; run 1, 10.0 sec., 307° C.

Fig. 89.—Saturation effect. I_M *vs.* length of excitation. Curve *A*, temperature 308° C.; curve *B*, temperature 267° C.; curve *C*, temperature 207° C.; curve *D*, temperature 155.5 C.; curve *E*, temperature 98° C.

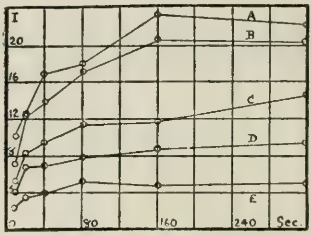

Fig. 89.

To get the maximum point in each run, smooth curves, not shown in the figures, were drawn through the different points. These curves show that increasing the excitation beyond a certain length does not increase the energy manifested as thermo-luminescence. That saturation takes place is further shown by the time that luminescence lasts. Figs. 87 and 88 show that the duration of luminescence has about reached a maximum. The areas included between the curves and the coördinate axes also show

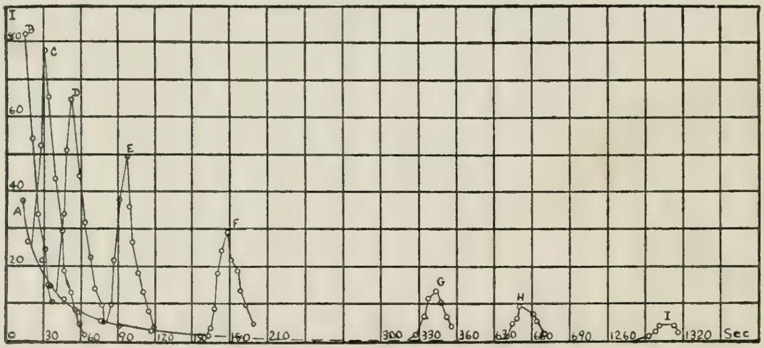

Fig. 90.

Effect of delay in heating. Time measured from the end of excitation. Excited 320 seconds at room temperature. Temperature of furnace 303° C. Curve *A*, decay at room temperature. The time between the end of excitation and the beginning of heating is as follows:
Curve *B*, 2.5 seconds; *C*, 21.4 seconds; *D*, 41.3 seconds; *E*, 81.1 seconds; *F*, 162.0 seconds; *G*, 321.6 seconds; *H*, 631.8 seconds; *I*, 1280.0 seconds.

that further increase with increased excitation is limited. The shifting of maximum intensity resembles an inertia effect; the longer the excitation the longer it takes the temperature to produce the maximum thermo-effect.

The effect of delay between the end of excitation and the beginning of heating was investigated at some length. The general character of the results obtained is given in Fig. 90 and the subsequent diagrams.

Fig. 90 shows the way in which the outburst of thermo-luminescence diminishes in intensity, in the case of a substance excited for a given time and subsequently heated in a furnace of given temperature, as the interval of time before the beginning of heating is increased.[1] Figs. 92 and 93, in which time is measured from the beginning of heating, indicate clearly a shift in the time of reaching the maximum of intensity of thermo-luminescence in the same direction as that already noted in the case of increased length of excitation. The energy of phosphorescence does not manifest itself so rapidly after long delay in heating or long excitation as after short delay or short excitation. For any given excitation and temperature the curves tend to coincide after a given time, which may be taken to indicate that the interval of time occupied by an outburst of thermo-luminescence is independent of the time which has elapsed since excitation.

Table 16 gives the approximate duration of the flash of thermo-luminescence from nine sets of observations under varying conditions of excitation and heating.

While the times stated are necessarily somewhat inaccurate, they indicate that brief outbursts follow short exposures and high temperatures of the furnace and *vice versa*.

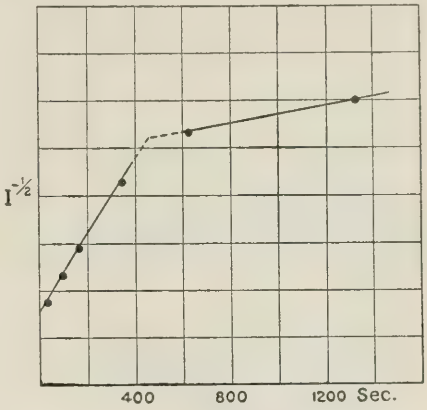

Fig. 91.[1]

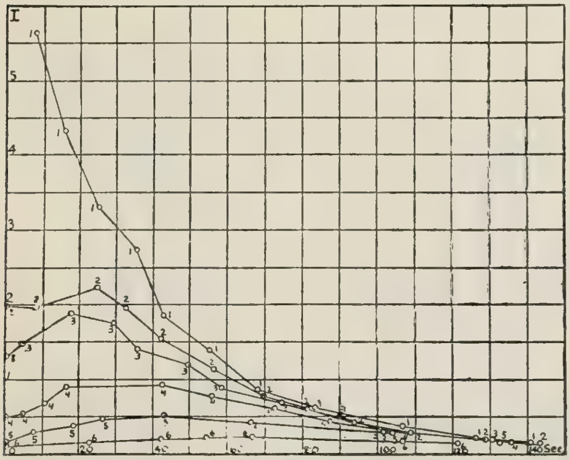

Fig. 92.

Effect of delay in heating. Time measured from beginning of heating. Excited 320 seconds at room temperature. Temperature of furnace 93° C. The time between the end of excitation and the beginning of heating is as follows: Curve 1, 2.0 sec.; curve 2, 21.9 sec.; curve 3, 41.5 sec.; curve 4, 81.5 sec.; curve 5, 162.0 sec.; curve 6, 332.0 sec.

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[1] The location of the crests *C, D, E, F, G, H, I* (Fig. 90) is along a curve which suggests in its form the ordinary curve of phosphorescence, and when we apply the usual criterion, *i.e.*, plotting $I^{-\frac{1}{2}}$ and times, we get the curve shown in Fig. 91, which has the significant form already discussed in Chapter IV of this treatise.

Fig. 94 gives in graphical form a summary of the results of nine sets of observations upon the decrease in maximum intensity of thermo-luminescence with delay in heating. The curve *G* is from data plotted in Fig. 90. In Fig. 95, which is from the same set of observations, the time of maximum intensity is measured from the beginning of heating in order to exhibit more clearly the shift of the maximum as the result of delay in beginning heating.

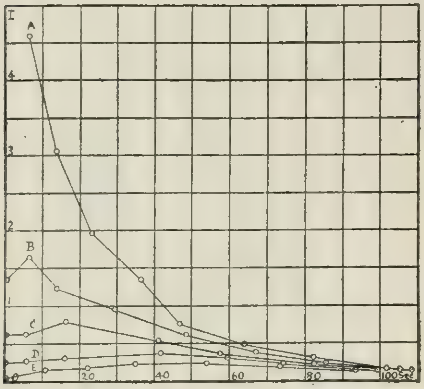


Fig. 93.

Curves similar to Fig. 93. Excited 40 seconds at room temperature. Temperature of furnace 94° C. The time between the end of excitation and the beginning of heating is as follows:
Curve *A*, 1.9 sec.; curve *B*, 22.1 sec., curve *C*, 42.1 sec.; curve *D*, 82.6 sec.; curve *E*, 162.1 sec.

TABLE 16.

Time of excitation.	Temp. of furnace.	Time required for intensity to reach I.	
sec.	°C.		sec.
10	94	$I=1.25$	60
10	200	"	45
10	302	"	32
40	92	$I=2.5$	100
40	200	"	80
40	300	"	37
320	93	"	120
320	202	"	75
320	303	"	40

In Fig. 96 is shown the maximum intensity plotted against length of excitation. These curves are similar to those shown in Fig. 89, but cover a larger range of conditions. They indicate the same tendency to saturation with increasing excitation whatever be the temperature and the delay of heating; a point which would undoubtedly have been better shown had a greater number of lengths of excitation been investigated.

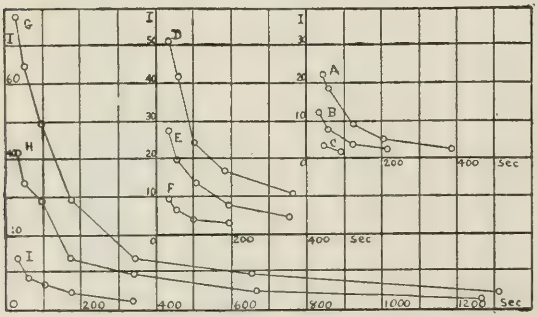


Fig. 94.

Decrease in maximum intensity with delay in heating. The coordinates are I_M and time of I_M measured from the end of excitation. The length of excitation and the temperature of the furnace are as follows:

Curve *A*, 320 sec., 93° C.
B, 40 sec., 92° C.
C, 10 sec., 94° C.
D, 320 sec., 202° C.
E, 40 sec., 200° C.
F, 10 sec., 200° C.
G, 320 sec., 303° C.
H, 40 sec., 300° C.
I, 10 sec., 302° C.

Fig. 97 shows the relation between maximum intensity and temperature for the nine sets of runs. These curves correspond to those shown in Fig. 84. In some of the cases but one point can be given, the other runs showing no measurable intensity or else no maximum. The relation between the maximum intensity and the temperature, beyond the fact that the intensity increases with the temperature, is not clear.

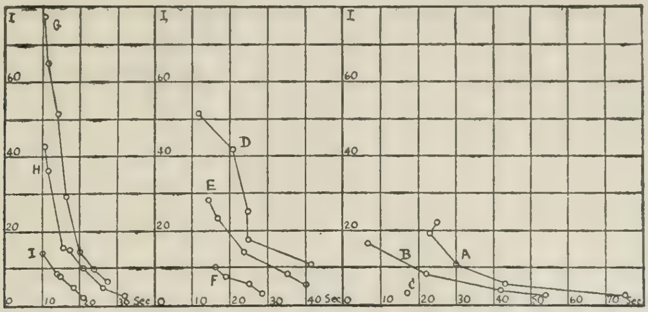


Fig. 95.

Maximum intensity *vs.* time of maximum intensity measured from the beginning of heating. For description of curves see Fig. 94.

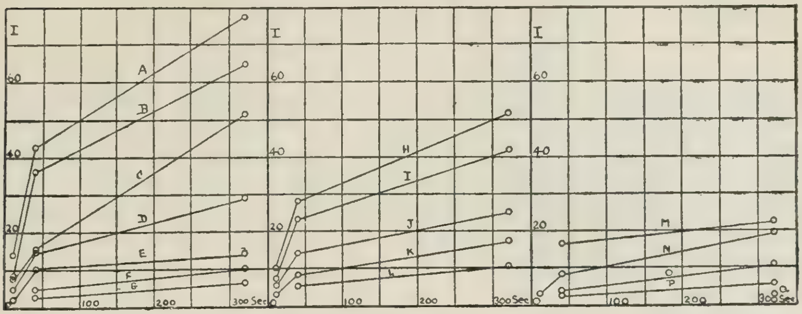
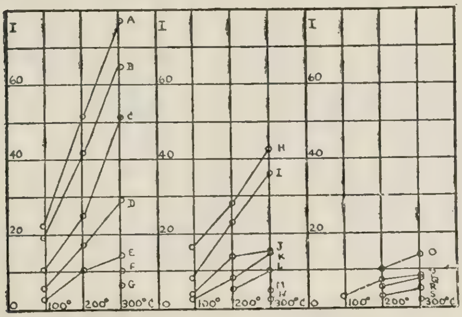


Fig. 96.

Maximum intensity *vs.* length of excitation. The temperature of the furnace and the time between the end of excitation and the beginning of heating are as follows:

Curve *A*,	302° C.,	21.6 sec.	Curve *H*,	200° C.,	21.9 sec.	Curve *M*,	93° C., 21.5 sec.
B,	"	41.7	*I*,	"	41.5	*N*,	" 41.8
C,	"	81.4	*J*,	"	81.6	*O*,	" 82.0
D,	"	161.6	*K*,	"	161.8	*P*,	" 162.0
E,	"	321.0	*L*,	"	321.7	*Q*,	" 322.0
F,	"	636.0					
G,	"	1155.0					



Curve *A*,	320 sec.,	21.7 sec.
B,		41.3
C,		81.3
D,		162.0
E,		321.8
F,		631.8
G,		1280.0
H,	40 sec.,	22.1 sec.
I,		41.8
J,		81.6
K,		161.9
L,		321.9
M,		642.0
N,		1230.0
O,	10 sec.,	21.8 sec.
P,		41.7
Q,		81.7
R,		161.4
S,		319.5

Fig. 97.

Maximum intensity *vs.* temperature of furnace. The length of excitation and time between end of excitation and beginning of heating are as shown herewith.

In an earlier paragraph mention was made of the existence of two bands in the phosphorescence spectrum of the sample of Sidot blende used in this study.

If there are two bands, it is natural to expect some indication of their existence in the curves of thermo-luminescence. Referring to Fig. 92, there will be found evidence of two bands. After the intensity has reached a maximum, it falls off rapidly at first, then there is an indication of a slowing up in the decay followed by relatively rapid decay. Whether there is a complete bending back in any of the curves can not be stated, because the points are too far apart. Whether a complete bending back is possible depends on the relative intensities of luminescence of the two bands and the relative rapidity of decay. It has not seemed advisable to search for more certain indications of two bands in the thermo-phosphorescence because of the difficulty of increasing the number of observations taken in a given time. In part II of this chapter, curves will be shown in the case of Balmain's paint, which decays slowly enough to be more completely studied. This substance has two bands in its phosphorescence spectrum, and the curves of thermo-luminescence show two maxima under certain conditions of excitation, temperature, and delay in heating.

EXPERIMENTS WITH BALMAIN'S PAINT.

In the experiments with Balmain's paint the apparatus used was the same as that used in the study of Sidot blende. A mercury lamp was used to excite the calcium sulphide, which was in powder form. Since the lamp was made of ordinary glass and the light from it was reflected at a mirror before reaching the powder, the excitation was chiefly due to the visible spectrum in the mercury arc. Before each excitation the powder was exposed to infra-red rays in an attempt to bring it to a standard condition.

The action of infra-red rays upon the phosphorescence of calcium sulphide is not so strong as upon Sidot blende. In the latter case, as has already been shown in Chapter V, phosphorescence due to a very long excitation can be destroyed almost immediately by infra-red rays, and only the highest allowable temperature, just under dull red heat, is able to produce thermo-luminescence without renewed excitation. In the case of calcium sulphide a very long exposure to infra-red rays was necessary to destroy the phosphorescence, and no exposure was found to be long enough to suppress the thermo-luminescence completely. At the beginning of the experiments on calcium sulphide this fact was not recognized. If it had been, the powder could have been brought to an approximately standard condition by heating to a temperature a little higher than the highest temperature at which thermo-luminescence was to be studied. Fortunately, in every case the powder was exposed for one minute to infra-red rays of constant strength, hence it was always brought to a semi-standard condition. No extended attempt was made to compare the two methods, since the blue phosphorescence of calcium sulphide is a difficult color to measure in the photometer.

The fluorescence spectrum of this sample of calcium sulphide is shown in Fig. 98. This curve was obtained by comparison with the light reflected from the surface of a block of magnesium carbonate illuminated by an acetylene flame. Two bands are indicated by the curve, one with a maximum at about 0.41μ and the other with a maximum at about 0.54μ.

The dotted vertical lines show the wave-lengths of the lines of the mercury arc. The figure indicates the presence of stray light in the spectro-photometer, which lowers the zero line with respect to the curve and unduly exaggerates the ratio of the maximum of the band at 0.41 μ to the maximum of the band at 0.54 μ. The band in the blue is, however, evidently much more intense than the other. This fact was shown by the color of the initial phosphorescence, which was blue.

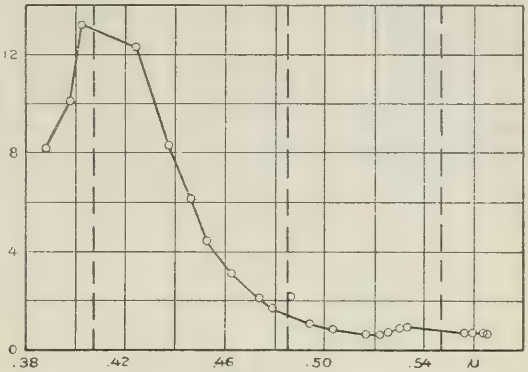


Fig. 98.

Fluorescence spectrum of calcium sulphide excited by the visible spectrum of a mercury arc.

The effect upon the decay curve of varying the length of excitation is shown in Fig. 99. These curves are plotted with distances of the standard light from the photometer as ordinates and time measured from the end of excitation as abscissas. For short excitations the curves are concave downward throughout, but for longer excitations the bending is concentrated in the first part of the curves. These curves are similar to those obtained with Sidot blende, except that the phosphorescence lasts much longer. Hence it is possible to get points relatively nearer the origin. This fact allows one to make a tentative deduction regarding initial intensity and length of excitation at room temperature. A study of Fig. 99 indicates strongly that the initial intensity is greater the longer the excitation, which is the impression obtained when getting the curves. Though it is impossible,

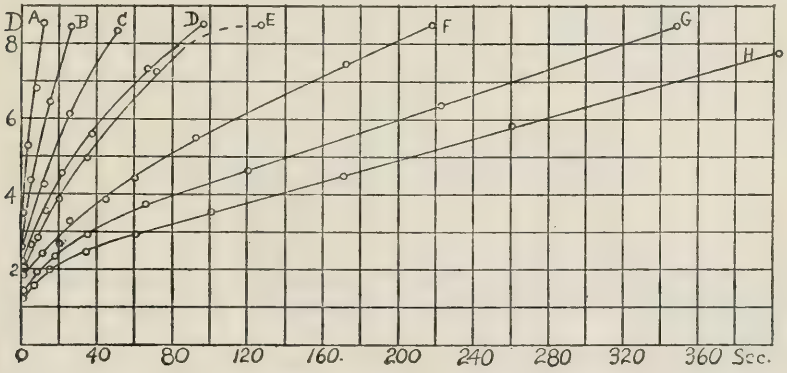


Fig. 99.

Effect of varying the length of excitation. Excitation and decay at room temperature.

Curve *A*, excited	14.4 sec.	Curve *E*, excited	59.9 sec.
B, "	30.1	*F*, "	150.3
C, "	30.1	*G*, "	300.0
D, "	60.2	*H*, "	600.0

Curves *A*, *B*, *D*, and *F* were taken on the second day and the remainder on the first day of the run.

with this apparatus, to get a measurement much nearer the origin than 0.8 of a second, yet the eye is sensitive to part of the change of intensity before this, giving one a means of estimating roughly the amount of change before the first measured point. The saturation effect is prominent, as was the case with Sidot blende. Saturation is shown both by the change of initial intensity and by the change in slope of the curves as the excitation is increased.

In Fig. 99 some of the curves were obtained one day and the remainder on another day. One would expect curves *B* and *C* to coincide. The difference between them is probably due to the fact that the infra-red exposure does not reduce the powder to a standard condition. Curves *D* and *E* agree more closely than *B* and *C*. A curve, not shown in the figure, excited for 300 seconds, coincides with *G*. This coincidence may have been due to chance, but it is what would be expected, because the effect of previous history becomes of less importance as the length of excitation is increased.

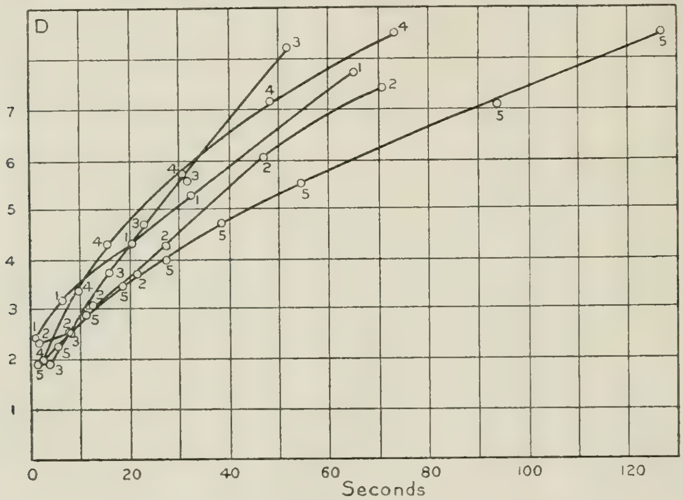


Fig. 100.

Decay curves at different temperatures. Excited 2 minutes.
Curve 1, temp. of excitation and decay, room temp.
2, " " " " " 66° C.
3, " " " " " 102°
4, " " " " " 145°
5, " " " " " 180°

That the lack of agreement of curves *B* and *C* is due to the previous history of the powder is substantiated by the fact that curve *A* was observed immediately before curve *B*, and curve *G* immediately before curve *C*. No deductions can be made for curves *D* and *E*, because the history of the powder previous to the excitation for curve *E* is not known. Curve *D* followed *B* immediately, but some preliminary work without infra-red was done before the infra-red treatment preceding curve *E*.

The changes produced in the decay curve by varying the temperature at which excitation and decay take place are shown in Fig. 100. The part that previous history plays in these curves can not be estimated accurately, but its effect is small, because the excitation, which is relatively a long one, was not changed during a set of curves. The curves were taken in the order that they are numbered. Curve 1, taken at room temperature, is similar to the typical decay curves shown in Fig. 99. As the temperature is raised the curves pass through a series of changes. Curve 2 begins concave upward, but changes during the decay to concave downward. Curve 3 is practically a straight line throughout. As the temperature is raised still farther, the curves again become concave downward throughout, differing not widely from the typical decay curves at room temperature.

Another set of curves similar to those in Fig. 100 is shown in Fig. 101, where the length of excitation is 10 minutes. The double bending[1] is again exhibited in curve 2.

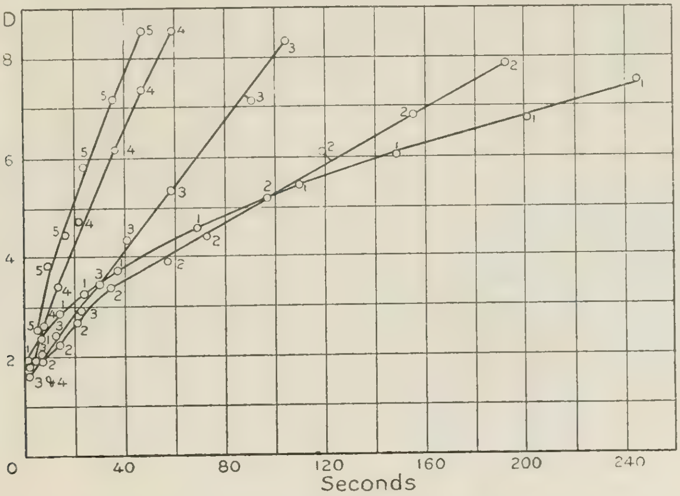


Fig. 101.

Decay curves at different temperatures. Excited 10 minutes.
Curve 1, temp. of excitation and decay, room temp.
2, " " " " " 42° C.
3, " " " " " 74°
4, " " " " " 101°
5, " " " " " 124°

The effect of previous history is shown in Figs. 102 and 103. These curves might readily be mistaken for curves showing the effect of varying the length of excitation. Fig. 103 also shows the effect of previous history, modified, however, with the effect of temperature.

The decay of phosphorescence in the case of Balmain's paint was studied some years ago by F. J. Micheli,[2] who has published decay curves of several phosphorescent substances, among them Balmain's paint. For the sake of comparison, several of these curves have been replotted in Figs. 105 and 106 with $1/\sqrt{I}$ and time as coördinates. Fig. 105 shows the effect of varying the length of excitation. Fig. 106 shows the effect of varying the tempera-

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[1] When taking the runs on which Fig. 99 is based, no importance was given to the single curve which shows double bending. Later, the runs on which Fig. 100 is based were made and the apparatus was rearranged for study of another substance before the significance of the double bending was recognized. On looking over all the curves taken on Balmain's paint, other indications of double bending were found, but none of them so pronounced as those shown above.

[2] Arch. des Sci. Phys. et Nat., 12, p. 5, 1901.

ture at which excitation and decay take place. These curves and the curves given earlier in this article agree generally. Fig. 106 shows the effect of excitation and decay at a temperature lower than any used in this article.

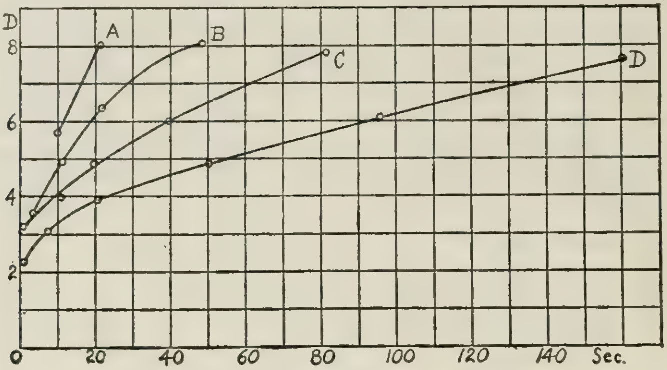

Fig. 102.

Effect of history previous to excitation. Excitation and decay at room temperature. Excited 30 seconds. Curve *A*, excited after action of infra-red; curve *B*, excited immediately after curve *A*; curve *C*, excited immediately after curve *B*; curve *D*, before exciting for curve *D*, the powder was excited for 10 minutes and allowed to decay to an intensity corresponding to D = 9 in the figure, at which time the excitation of 30 seconds was begun.

In the case of calcium sulphide, it is not necessary to use a spectrophotometer to prove that there is more than one band included in the phenomenon of phosphorescence, for under the influence of heat the color of the powder can be seen to change from blue to green.

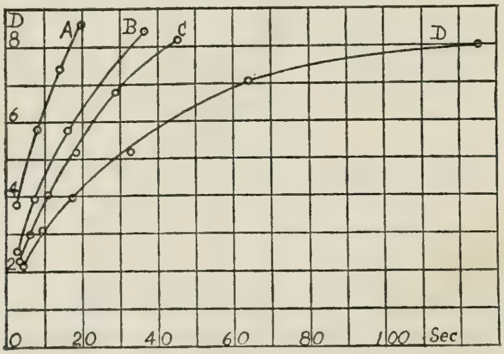

Fig. 103.

Curves of Fig. 102 repeated at a temperature of 133° C.

It has already been shown that the form of the phosphorescence decay curve may be closely approximated on the basis of two bands, each following the law

$$I = \frac{1}{(a+bt)^2}$$

This explanation was carried to some length in the earlier part of this chapter. But there seems to be no way of combining two decays, each of which follows this law so as to produce an upward bending. If it be supposed that one band increases in intensity as the other decreases, then an upward bending is possible; but a downward bending is impossible unless both the bands subsequently decay together. This suggests that one of the bands may be due to some secondary effect, instead of being produced by the exciting light. Such a band would increase in intensity a certain length of time, then decrease in intensity. If we suppose that the first band follows the law suggested, and that the second band follows the same

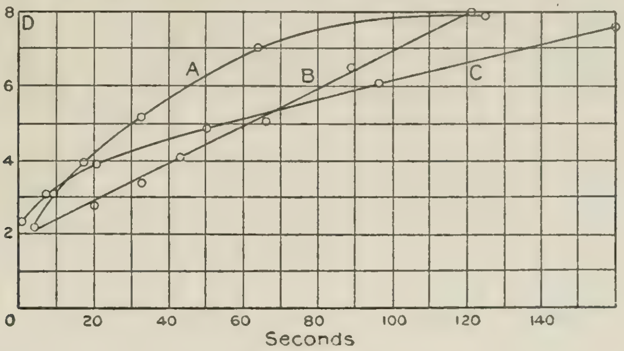

Fig. 104.

Effect of history previous to excitation. Excited 30 seconds. Before each excitation the powder was excited for 10 minutes and allowed to decay to an intensity corresponding to $D = 9$, at which time the excitation of 30 seconds was begun.

Curve *C*, excitation and decay at room temp.
B, " " " " 88° C.
A, " " " " 133°

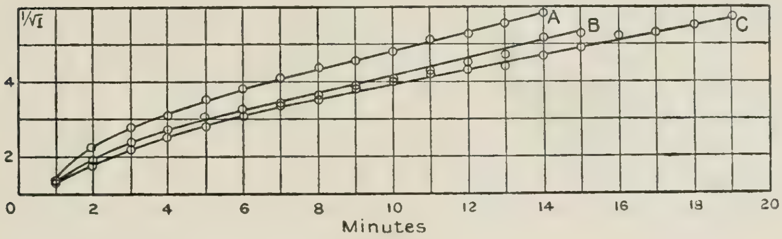

Fig. 105.

Effect of varying the length of excitation. Excitation and decay at a temperature of 18° C. (replotted from data of Micheli).

Curve *A*, excited 5 seconds; *B*, 20 seconds; *C*, 300 seconds. Another curve excited for 60 seconds coincided almost exactly with curve *C*.

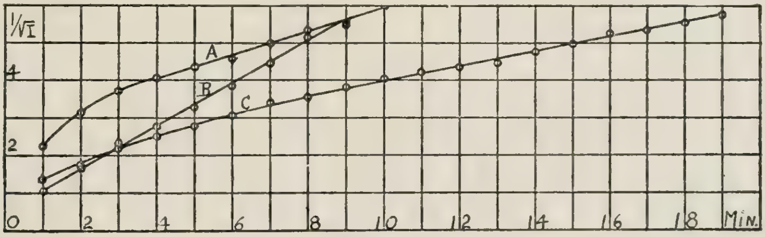

Fig. 106.

Effect of varying the temperature at which excitation and decay take place. Excited 300 seconds (replotted from data of Micheli).

Curve *A*, temp. of excitation and decay, −21° C.
B, " " " " " 100°
C, " " " " " 18°

law after it has reached its maximum intensity, then the discussion previously given still holds good, the supposition being that the second band is completely formed before the first point on a curve can be measured. If, however, conditions can be changed so that a point can be observed before the second band is completely formed, then the curve will show initially an upward bending, as in curve 2, Figs. 99 and 100. If a band is formed by some secondary effect it will usually be present in the fluorescence spectrum because the excitation is continued long enough for the band to be formed.

The effect of previous history can be explained without adding any complications to the ideas already set forth. In the case of Sidot blende, it was undoubtedly the band of longer wave-length that decayed more slowly. The same is true, probably, for calcium sulphide, for the color changes from blue to green when the powder is heated. In the case of the decay curve at room temperature, the intensity is too small for the change in color to be recognized by the eye. Assuming that the band of longer wave-lengths decays more slowly, and that this band is due to some secondary effect, then the action of repeated excitations without intervening treatment with infra-red might be to increase the intensity and to decrease the rapidity of decay of the second band without introducing any change in the rapidity of decay of the first band. Some indications of these effects can be seen in Figs. 101 and 102.

It is unfortunate that the curves in Figs. 101 and 102 were not taken in the reverse order, *i. e.*, excitation of long duration followed by shorter excitations. Such curves, according to the ideas just set forth, should show parallelism after the decay had proceeded some time. Several of the sets of curves described in Chapter IV were taken in this order and they exhibit parallelism after decaying a short time. To explain completely the curves in Figs. 99 and 100 on the basis of a second band due to secondary causes is impracticable, because the problem is complicated by the addition of the effect of temperature. One assumption will necessarily have to be added, *i. e.*, that there are certain temperatures at which either one or the other of the bands is most readily formed. This is a possible explanation of the fact that the decay curve becomes a straight line at one temperature.

A number of sets of observations were made to show the effect of heating after decay has begun. In these experiments the powder was exposed to infra-red rays, then excited and allowed to decay at room temperature, heating being begun at a definite point on the decay curve. Figs. 107 and 108, in which the coördinates are intensity and time, show the effect of varying the length of excitation. The double flash mentioned in the case of Sidot blende is plainly evident in the curves, and in the experiment it was evident to the unaided eye. The color also varied, being blue for the first flash and a yellowish green for the second. At the longest excitation the second flash is barely visible in the photometer, the only evidence of its existence being a slowing up in the rate of decay. As the length of excitation is decreased, the second flash becomes, relative to the first, greater and greater.

At lower temperatures the second flash becomes less evident, and this peculiarity of the curve for 600 seconds excitation, as shown in Figs. 107 and 108, no longer exists. For the lower temperatures the second flash for

600 seconds excitation is greater than that for any shorter excitation at the same temperature. At a temperature near 100° C., the second flash is no longer evident in the curves.

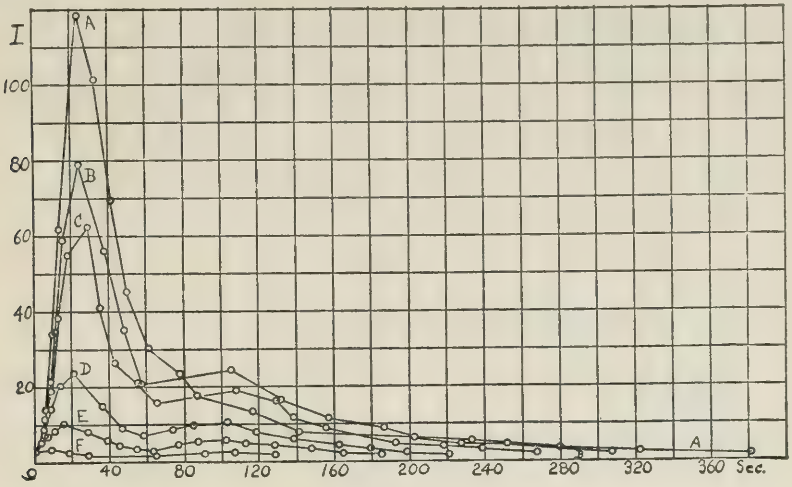

Fig. 107.

Effect of varying the length of excitation. Excited and allowed to decay at room temperature to $I = 2.9$, when heating was begun. Temperature of furnace, 277° C.

Curve *A*, excited 600.2 sec. Curve *D*, excited 60.7 sec.
B, " 300.0 *E*, " 30.1
C, " 150.1 *F*, " 14.8

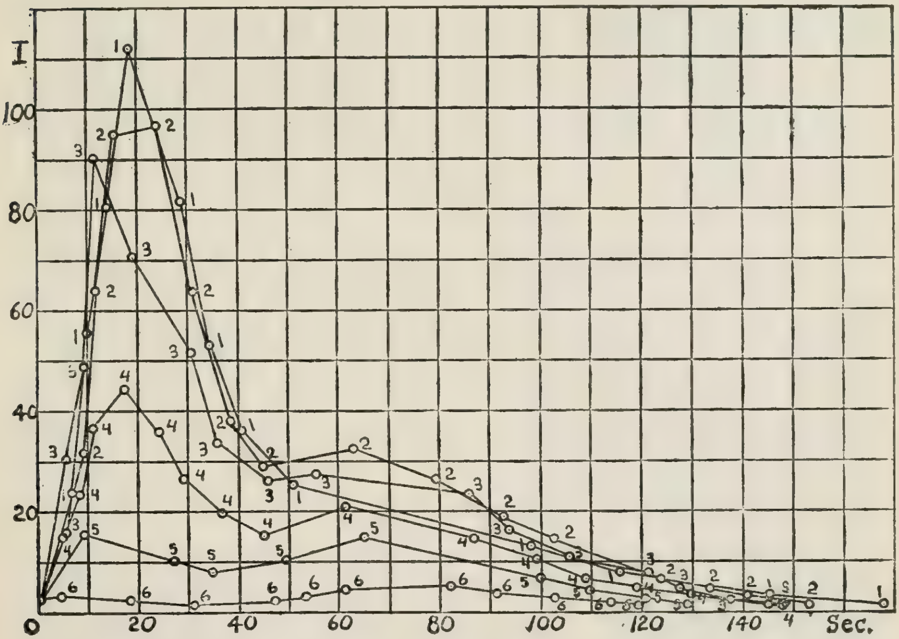

Fig. 108.

Curves similar to Fig. 107. Temperature of furnace, 339° C.

Curve 1, excited 600.0 sec. Curve 4, excited 59.8 sec.
2, " 300.0 5, " 29.8
3, " 150.1 6, " 14.2

It is evident that two bands are represented in the preceding curves. Any one of these curves is probably made up by the superposition of two curves, each of these component curves representing the flash for one of the bands. If one considers the first flash in Figs. 107 and 108, it will be seen that the curves resemble closely corresponding curves obtained with Sidot blende. The maximum intensity increases with length of excitation and occurs later and later. The areas included between the curves and the coördinate axes increase with the excitation. The effect of saturation is shown both by the change in areas and by the change in the maximum intensities. The observations have been plotted in Fig. 109 so as to show the relation between maximum intensities and lengths of excitation, in which case if one considers the first flash alone the curves are similar to those already given for Sidot blende. The effect of changing the temperature of the furnace is shown in Fig. 110.

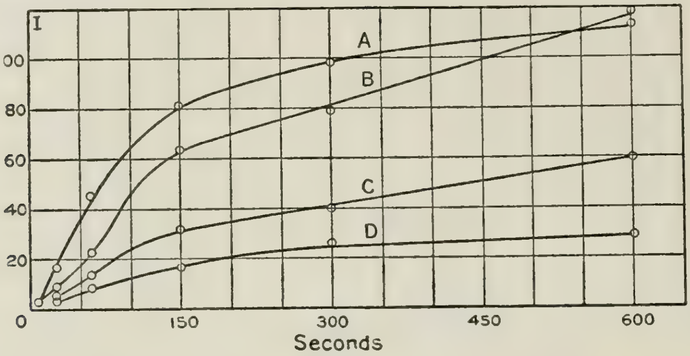

Fig. 109.

Maximum intensity of the first flash plotted against length of excitation.
Curve 1, temp. of furnace 339° C. (from Fig. 108).
2, " " " 277° (from Fig. 107).
3, " " " 222°
4, " " " 148°

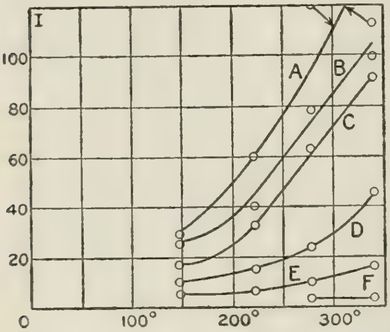

Fig. 110.

Maximum intensity of the first flash plotted against temperature of the furnace.
Curve *A*, excited 600 sec.
B, " 300
C, " 150
D, " 60
E, " 30
F, " 15

The second flash does not always follow the laws of the first flash, as can be seen in Fig. 108. As the length of excitation is increased, the maximum intensity of the first flash occurs later and later, while the maximum of the second flash occurs earlier and earlier. This effect is not well defined in Fig. 107, due perhaps to the fact that the flash is of smaller intensity and consequently more difficult to follow accurately. The effect of saturation in the case of the second flash is shown in Fig. 111. These curves indicate that an increase in the length of excitation beyond a certain length does not increase the maximum intensity, but decreases it.

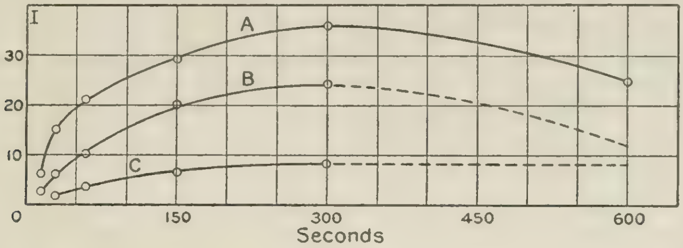

Fig. 111.

Maximum intensity of the second flash plotted against length of excitation.
Curve *A*, temp. of furnace, 339° C. (from Fig. 108).
B, " " " 277° (from Fig. 107).
C, " " " 222°

The relation between the maximum intensity of the second flash and the temperature is shown in Fig. 112. This figure corresponds closely to Fig. 110, which shows the corresponding relation for the first flash.

Fig. 113 shows the effect of delay in heating and Fig. 114 the same

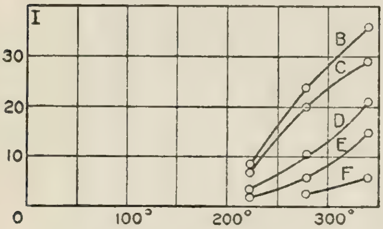

Fig. 112.

Maximum intensity of the second flash plotted against temperature of the furnace.

Curve *B*, excited 300 sec.
C, " 150
D, " 60
E, " 30
F, " 15

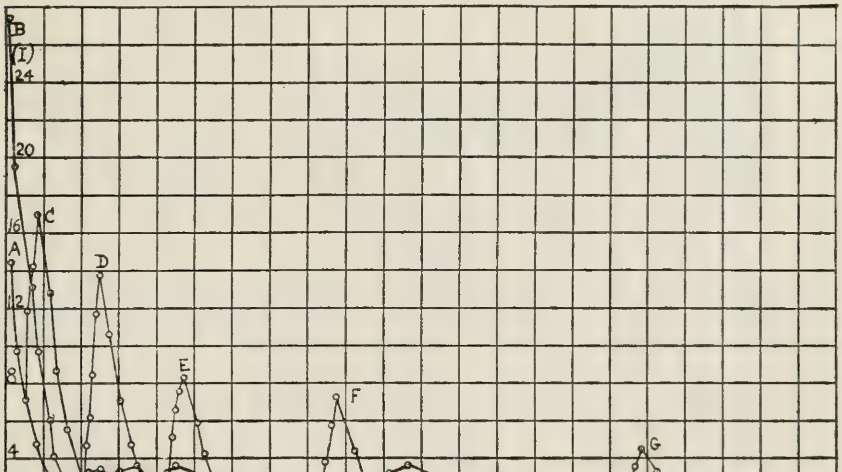

Fig. 113.

Effect of delay in heating. Time measured from end of excitation. Excited 60 seconds at room temperature. Temperature of furnace, 228° C. Curve *A*, decay at room temperature. The time between the end of excitation and the beginning of heating is as follows: Curve *B*, 2.1 seconds; *C*, 25.6; *D*, 101.7; *E* 203.2; *F*, 401.7; *G*, 801.7.

curves plotted with time measured from the beginning of heating. Here again, if one considers the first flash alone, the curves are similar to those shown in the case of Sidot blende. The longer the delay in heating, the less intense the flash and the later the maximum intensity of each flash. Furthermore, the time of decay at one temperature and constant length of excitation is constant. It is difficult to make any deduction from the points representing the second flash.

Another set of curves similar to those shown in Fig. 113 is shown in Fig. 115. These curves show that the second flash becomes relatively larger with respect to the first as the excitation is shortened, and under suitable conditions, as in curve *C*, may become considerably larger than the first.

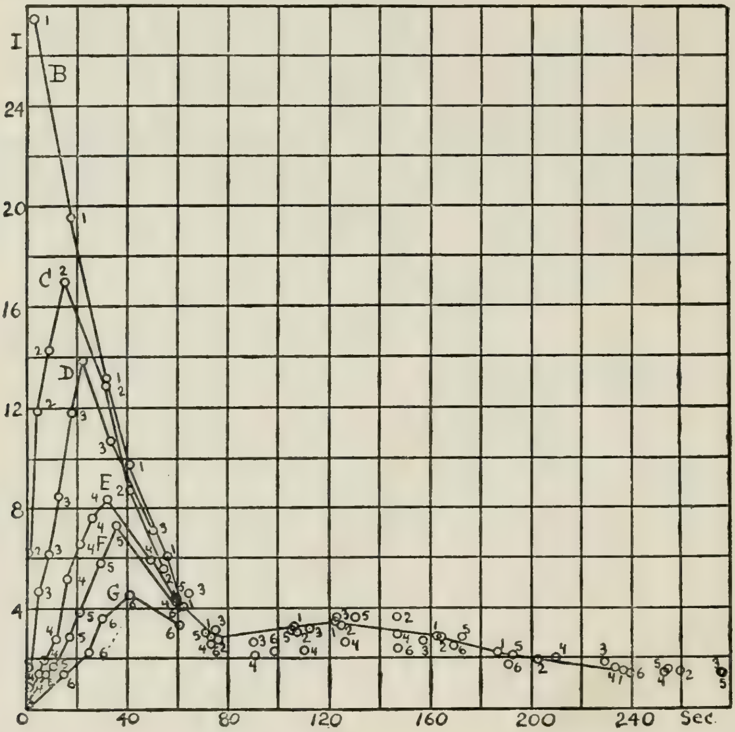

Fig. 114.

Effect of delay in heating. Time measured from the beginning of heating. Same curves shown in Fig. 113.

It is difficult to say how much difference exists between the behavior of Sidot blende and Balmain's paint. The decay curves at room temperature are very much alike. As the temperature is raised both decay curves become straight lines, but Balmain's paint shows a transition through a double curvature decay before reaching the straight line decay, while Sidot blende does not exhibit this phenomenon. Above the temperature at which the decay curve becomes straight, Balmain's paint shows a decay approximating the decay at room temperature, while in the case of Sidot blende the decay is too rapid to be followed with the available apparatus. The decay of Sidot blende is so rapid that one can not get enough points on a curve to say positively that it does not exhibit double curvature at high temperatures. In the cases where the powder is heated after excitation, Balmain's paint shows a double flash under some conditions, and one flash under other conditions, while Sidot blende shows one flash under all conditions, unless it be admitted that there are indications of a double flash in some of the Sidot-blende curves, in which case the two substances show substantially the same curves. Considering the first flash only, there is perfect agreement between the curves of Sidot blende and Balmain's paint. The action of infra-red is more marked in the case of Sidot blende, but otherwise there is no marked difference. The fluorescence spectrum shows two bands in the case of each substance, but there is one point of difference, in that the band of shorter wave-length is more prominent in the case of Balmain's paint and less prominent in the case of Sidot blende than the band of longer wave-length.

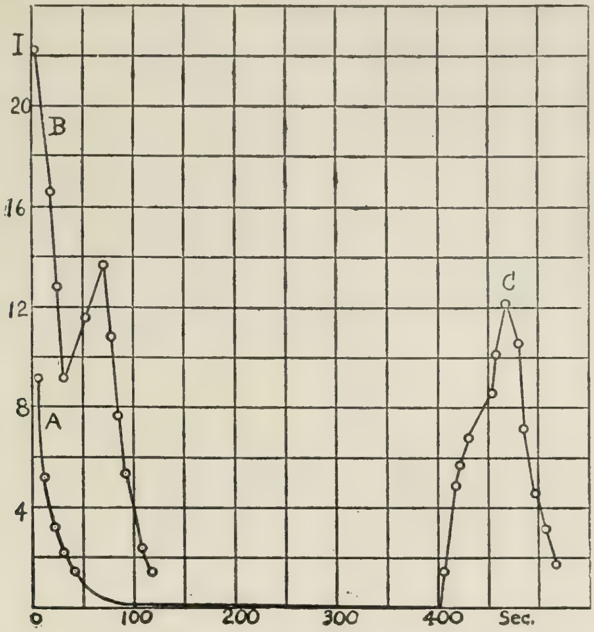

Fig. 115.

Effect of delay in heating. Time measured from the end of excitation. Excited 30 seconds at room temperature. Temperature of furnace, 338° C.
Curve *A*, decay at room temp.
B, waited 2 sec. after excitation before heating.
C, waited 400 sec. after excitation before heating.

CHAPTER VII.

STUDIES OF PHOSPHORESCENCE OF SHORT DURATION.

By the methods described in Chapters IV and VI of this memoir it is difficult to make observations of phosphorescence within less than 0.4 second of the close of excitation. This suffices for the determination of the form of the curve of decay with the exception of the region very near the origin. There are, however, many substances exhibiting brilliant initial phosphorescence where the effect fades to unmeasurably small intensity within a few hundredths of a second.

It is of considerable interest and importance not only to determine the curves of decay of such substances, but also, since Lenard[1] in a recent paper has questioned the linear relation between $I^{-\frac{1}{2}}$ and time during the so-called first process of decay, to study the earliest portions of the first process in the case of phosphorescence of slow decay.

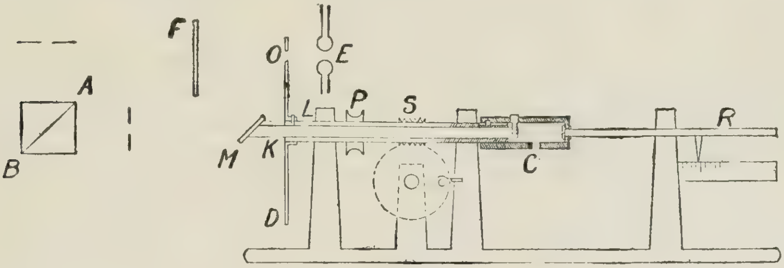

Fig. 116.

Messrs. Waggoner and Zeller at our suggestion have investigated these questions at some length, using a new type of phosphoroscope of especial design and working independently of each other. The present chapter contains a summary of their researches.

DR. WAGGONER'S STUDIES IN PHOSPHORESCENCE OF SHORT DURATION.[2]

METHODS OF MEASUREMENT.

The phosphoroscope used in these measurements is shown in Fig. 116. It consists of a disk *D*, fastened to a cylinder *L*, rotating about a horizontal axis. On the inside of *L* is a shaft *K* which rotates at the same speed as the cylinder. On the end of *K* is a plane mirror, placed 45° to the axis of the shaft, and by use of the mechanism at *C* the position of the mirror, relative to any point on the disk *D*, may be shifted while the disk is rotating. The disk has an opening at *O*, through which the light from the spark *E* may pass at each successive revolution and excite the specimen placed at *F*. If the mirror is in the position shown it will reflect into the slit of a spec-

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[1] Lenard, Annalen der Physik, XXI, p. 641, 1910.

[2] C. W. Waggoner, Physical Review, XXVII, p. 209.

trophotometer the light which comes from the phosphorescent screen F while it is being excited by the spark. By moving the rod R the mirror is turned so as to reflect the light from the screen F into the spectrophotometer some time after excitation, and in this way the intensity of the phosphorescence after successive excitations may be measured by the spectrophotometer AB. The cylinder L is driven by a motor belted to it over the pulley P. S is a worm driving a cog wheel, which serves as a device for recording the speed by making an electric connection with a chronograph once in every hundred revolutions of the disk. Current for the motor was taken from a direct-current source having a special device for maintaining constant voltage, and the speed of the motor was found to remain almost constant. The disk D has a second half-disk fastened to the first (not shown in the figure) by which it is possible to change the size of the opening at O. The essential advantage of this phosphoroscope over others is that the decay of the phosphorescent light may be studied without changing the time of excitation. Another feature of this method is that settings on the spectrophotometer for any curve may be repeated as often as desired and the time taken for the determination of each setting may be as long as desired. The results shown in the curves that follow were determined from two different settings of the spectrophotometer for each point, and the plotted point represents the average.

The source of excitation was the spark between iron terminals. To produce this spark an induction coil was connected to a source of alternating current of 60 cycles frequency, a small condenser being connected in multiple with the spark gap. In order to study the effect of decreased time of excitation, it was found necessary to increase the frequency of the spark, this being accomplished by connecting it to a source of alternating current giving 140 cycles. With this higher frequency the chances of the spark exciting the screen at each turn of the disk is greater; the higher frequency spark was also used as a check on the curves taken at the lower frequency.

The light from an incandescent lamp connected to a constant potential source was used for comparison in the spectrophotometric measurements.

METHODS OF PREPARING THE PHOSPHORESCENT COMPOUNDS.

The phosphoroscope just described, although it has a considerable range as to speed, is especially adapted to compounds whose phosphorescence decays rapidly. A number of such compounds were prepared and were studied along with several specimens of willemite whose decay was of suitable rapidity.

In preparing the compounds the methods given by Wiedemann and Schmidt[1] and Andrews[2] were followed. The ease with which these compounds may be prepared and the intensity of the phosphorescent light given off when they are excited by the spark seem to warrant a rather detailed account of their preparation.

$ZnCl_2+MnSO_4$.[3]—Some zinc chloride prepared from metallic zinc was dissolved in a small quantity of distilled water. A small trace (usually less

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[1] Wied. Ann., 54, p. 604, 1895.

[2] Science, XIX, March 1904.

[3] $MnSO_4$ was selected as an active salt in a number of cases, since it has been found by Lenard and Klatt (Annalen der Physik, 15, p. 243, 1904) that with this salt the intensity of phosphorescence is less affected by varying the concentration than with any other active agent.

than 1 per cent) of $MnSO_4$, dissolved in water, was added to the $ZnCl_2$ solution and the whole brought to the boiling point. An equal volume of sodium silicate, as the flux, was then added and the whole evaporated to dryness. On being exposed to the spark, faint green phosphorescence could be seen. It was then placed in a porcelain crucible and heated to a bright red for 2 hours. When cool it showed pale green fluorescence when exposed to the spark, and when the exciting source was cut off it was found to have considerable bright green phosphorescence. A sample of the powder at this point was kept and marked $ZnCl_2$ No. 1. The remainder of the powder was heated to a bright red for 3 hours and when cool showed both fluorescence and phosphorescence of greater intensity than did $ZnCl_2$ No. 1. A sample of this was saved and marked No. 2. The remaining powder was heated 2 hours at a bright red; on examination when cool it was found to have lost some of its original phosphorescent intensity. This was marked $ZnCl_2$ No. 3.

$CdCl_2+xMnSO_4$.—Substituting $CdCl_2$ for $ZnCl_2$, but giving it exactly the same treatment, it was found that it was necessary to heat the compound at a bright red for 3 hours before the phosphorescence was very intense, and that subsequent heating had no marked effect on its phosphorescent intensity when exposed to the spark. The fluorescence was pink and the phosphorescence dark red.

$CdSO_4+xMnSO_4$.—Some $CdSO_4$ was dissolved in water with a small trace of $MnSO_4$ and the whole heated to dryness without adding the flux. The resulting white powder showed pale yellow fluorescence, and an orange yellow phosphorescence of much longer duration than the zinc compounds.

$ZnSO_4+xMnSO_4$.—$ZnSO_4$ substituted for $CdSO_4$ and treated in the same way resulted in a white powder which showed pink fluorescence and bright red phosphorescence, but the intensity was too small to be measured by the method used.

Some "chemically pure" calcium sulphide was purchased with the view of trying to prepare compounds of CaS and $MnSO_4$, but it was found to be already an active phosphorescent compound having a brownish-red color.

Two large pieces of willemite, showing brilliant green phosphorescence with the iron spark, were studied. It was found that their rates of decay were not the same. The sample having the slowest decay was marked willemite No. 5. The sample having the very rapid decay was crushed into a fine powder, a sample made into a screen and marked willemite No. 1. Part of the powder was heated to a bright red heat in a porcelain crucible for 45 minutes. This was marked willemite No. 2. The remainder of the powder was heated for 2 hours at a bright red, and marked willemite No. 3.

One $ZnCl_2+xMnSO_4$ sample made by W. S. Andrews, Schenectady, N. Y., was also studied.

For purposes of study, screens were made by placing the phosphorescent powder on small squares of heavy dark brown cardboard, the cards having been covered first with white "zapon" varnish.

Among the preparations just described was one of cadmium sulphate and manganese sulphate made by simply evaporating to dryness a water solution of the two salts. After studying this compound it was put aside for several months and when taken up later for further work it had lost its power of phosphorescence under excitation by the iron spark, but on being heated it regained its former brilliancy. This led to the suspicion that these simple salts are photo-luminescent only when in the anhydrous condition, and subsequent tests showed this to be true of all the compounds studied.

The fact that moisture affects the photo-luminescence of cadmium salts may be shown by exciting the anhydrous phosphorescent compound by an ultra-violet source and allowing the light to decay for several seconds. Now if a drop of water be placed on the decaying compound the residual light will flash out brilliantly for an instant and then disappear very rapidly. It was first thought that this phenomenon was due to the changes which take place within the salt as it takes up water of crystallization. The thermo-phosphorescence of the cadmium compounds, however, is quite marked, and Dr. Kortright, of the Department of Chemistry, West Virginia University, suggested that the effect might be partly due to thermo-phosphorescence brought about by the heating which accompanies the process of hydration. To obtain some idea of the rise in temperature, several grams of anhydrous salt were placed in a test-tube with a thermometer, and water was added. The rise of temperature was found to be as much as 5° C., which would account in a large measure for the phenomenon purely on the basis of thermo-phosphorescence. Alcohol, which is not a solvent for cadmium sulphate, was tried, but gave no effect.

The fact that these cadmium compounds do not show photo-luminescence when in the crystalline state led the writer to try some of the original cadmium sulphate from which the compounds with manganese were made; and when the water of crystallization was driven off, the salt was found to be highly phosphorescent. The color of the phosphorescence was similar to that when a manganese salt had been added, but was less intense. When subjected to kathode rays the sulphate showed more brilliant fluorescence but less phosphorescence than when excited by the spark.

An attempt was first made to purify the original cadmium sulphate by forcing it out of water solution with sulphuric acid, but this treatment increased rather than decreased the intensity of phosphorescence.

Another method was to precipitate the cadmium with hydrogen sulphide as cadmium sulphide, wash it with water till free from sulphates, then redissolve the sulphide in sulphuric acid, crystallizing the salt formed. This sulphate still gave a brilliant yellow phosphorescence under both the iron spark and the kathode rays.

The next method was to crystallize the salts in fractions from water which was slightly acidified with sulphuric acid to prevent hydrolysis. The mother liquor was saved in this case and the crystals redissolved and crystallized out. It was found that the phosphorescence of the successive crystals, as they separated out from the retained mother liquor, decreased rapidly in intensity and at the end of the seventh fractionalization was almost nil, thus indicating the presence of an impurity less soluble than the cadmium sulphate. This view was supported by a micro-chemical test made by Dr. Wilkinson[1] showing the presence of sodium and a slight trace of zinc.

In casting about for a cadmium sulphate free from phosphorescence numerous samples were tried and it was found that the "tested purity" cadmium sulphate made by Eimer and Amend was free to a remarkable

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[1] Journal Physical Chem., XIII, p. 719, 1909.

degree. The phosphorescence, under the iron spark, of the anhydrous powder was so small that it was necessary to stay in the dark room a long time before the eye became sensitive enough to detect the phosphorescence at all; and even then one could not be sure of the color. The analysis of this material given on the bottle was as follows: "Cd, 52.84 per cent; SO_3, 47.15 per cent; As, none; Zn, none." This material was tested by the kathode rays and it was found to show neither fluorescence nor phosphorescence.

That a zinc salt, when added to a cadmium salt, or vice versa, would produce a phosphorescent compound has been pointed out by Wiedemann and Schmidt.[1] This fact led to the suggestion that the presence of small traces of zinc in cadmium salt, or vice versa, might be detected by the photo-phosphorescence which these compounds show, and some rough tests were made showing photo-phosphorescence with less than one part of zinc sulphate in 10,000 parts of the phosphorescent-free cadmium sulphate. The phosphorescent color was green, but the intensity was not so great as when a sodium salt is added to a cadmium salt.

The pure cadmium sulphate is very susceptible to a small impurity; how susceptible will appear from the following experiment: Some water, which was twice distilled in an all-glass still, was placed in a bottle and allowed to stand over night. The following day this water was used to dissolve some of the pure cadmium sulphate and was then driven off. When the cadmium sulphate was tried under the ultra-violet source it was found to be highly phosphorescent. 200 c.c. of this same water when evaporated down in a platinum dish left a residue so small that it could not be seen except when the platinum dish was at red heat.

Cadmium Sulphate–Sodium Compounds.—Starting with the phosphorescence-free cadmium sulphate, a series of preparations was made by the addition of various salts of sodium. The method used was that already described. It was to dissolve the crystals of sodium salt and cadmium sulphate in water; slowly evaporate the solution to dryness, and test the compound for phosphorescence, when it reached the temperature of the room, by exciting by the iron spark. The compound, from the original crystals to the final test, was kept in a large platinum dish and every precaution was taken to prevent impurities from entering the solution.

The water was twice distilled in an all-glass still and used immediately in order to prevent it from taking up sodium from the glass container. To produce an even and easily regulated temperature a small electric furnace was made by wrapping "nichrome" ribbon around a porous battery cup; this proved to be a very satisfactory arrangement, for the platinum vessel could be placed inside of this furnace and covered over lightly to prevent impurities entering from the air while evaporation was taking place.

Only readily soluble salts of sodium were used; and each one was tested in the anhydrous condition for the presence of phosphorescence. In one or two cases it was necessary to recrystallize the salt to free it from the impurity causing the phosphorescence. Several different percentages of cadmium and sodium were tried and it was found that the intensity of phosphorescence depended somewhat upon the percentage of sodium present; but so far as the tests were carried no change was produced in the color

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[1] Wied. Ann., vol. 56, 1895.

of phosphorescence by rather wide variations in the percentages of the added sodium. In most cases of the compounds recorded in Table 17 the amount of sodium salt present was not far from 1 per cent.

An inspection of Table 17 shows that the color of the phosphorescence of cadmium salts with sodium ranges from blue to yellow. In all but two cases the intensity was very small—so small as to make it impossible to obtain from these compounds reliable curves of decay with a spectrophotometer. Doubtless all of these could be increased in intensity by finding the suitable proportion of sodium.

TABLE 17.

Sodium salt added.	Phosphorescent color.	Spectrum.
Na_2SO_4	Yellow.	
$Na_2S_2O_3$	No phosphorescence.	
Na_2SiO_3	Blue.	0.486μ, max...510μ, 0.604μ
$NaHPO_4$	Faint green.	
$NaNO_3$	Faint yellow.	
Na_2MnO_4	Greenish yellow.	.522μ, max...566μ, .616μ
$NaFl$	Greenish yellow.	.474μ, max...574μ, .612μ
Na_2CrO_4	No phosphorescence.	
$NaOH$	No phosphorescence.	
$NaCl$	Green.	.510μ, max...——, .580μ
$NaClO_3$	Faint yellow.	
Na_2CO_3	No phosphorescence.	
$NaBr$	Blue.	.414μ, max...480μ, .600μ
$Na_2B_4O_7$	Pale green.	
Na_2CrO_7	No phosphorescence.	
$Na_2SO_4Al_2(SO_4)_3$	Faint green.	

DISCUSSION OF RESULTS.

The results of the study of the substances just described are indicated by means of decay curves plotted, like many of those which appear in Chapters IV and VI, with $I^{-\frac{1}{2}}$ as ordinates, and times, counted from the close of excitation, as abscissas. It will be seen that the curves have the same general characteristics as those obtained by the measurement of long-time phosphorescence. They may be regarded as consisting of two straight lines merging into one another.

The curves in Fig. 117 are decay curves typical of three of the substances studied. In the case of curve A (willemite No. 5) the decay was so rapid that it was difficult on account of the small intensity of the light to follow the "second process" very far.

In each curve one point has been plotted to the left of the zero on the ordinates. This observation is made on the fluorescent light, *i. e.*, it is the intensity of the light coming from the screen when the mirror is in position to reflect the light which comes from the screen during excitation. The zero point, or the point where the exciting light fails to be reflected into the spectrophotometer, was determined by placing a piece of white paper in place of the screen.

Since the induction coil furnished at most 120 discharges per second it will be seen that, for the time of excitation employed in the measurements illustrated in Fig. 117, three sparks per revolution of the disk is the maximum number that could pass while the screen is exposed. It would seem then that the excitation might be uncertain and irregular. These excitations, however, follow each other very rapidly; for example, in curve *B*, Fig. 117, the rotating disk makes a complete revolution in 0.108 second, and since 10 to 20 seconds were required to make a setting of the spectrophotometer, whatever changes take place in the spark during successive excitation, the reading is an average value of the intensity at that point. In order to make sure of this, readings were taken starting with the lowest intensity and ending with the highest, then starting with the highest and following the decay to the lowest value of intensity, the points plotted being an average of the two settings for each point on the curve.

If the substances here studied exhibit the same hysteresis phenomena that have been found in Sidot blende and several other substances,[1] the decay curves obtained by this method are probably not the same as would be observed if it were possible to restore the substance to a standard condition between successive periods of excitation, for example by the action of infra-red rays. In using these curves to test any theory of the decay of phosphorescence, this fact must of course be taken into consideration.

The curves in Fig. 118 indicate a much slower decay than those shown in Fig. 117. The initial decay or first process, however, is quite rapid. These curves were more difficult to obtain, since the maximum of intensity lay in the yellow-red, while the substances whose curves are given in Fig. 117 have a green phosphorescence. On this account the points are less accurately determined than in Fig. 117. It is evident, nevertheless, that the curves have the same general character and consist of two straight lines merging into each other.

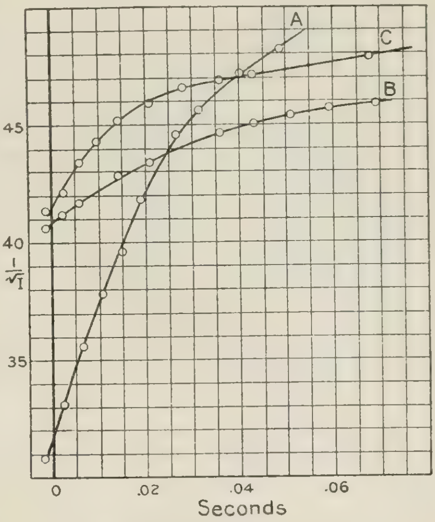

Fig. 117—Decay curves.

Curve *A*, Willemite No. 5, time of excitation 0.026 second.
Curve *B*, Andrews ZnCl$_2$, time of excitation 0.027 second.
Curve *C*, ZnCl$_2$ No. 3, time of excitation 0.26 second.

All the substances mentioned in this chapter are excited to fluorescence by kathode rays. The mixture containing CdSO$_4$ was especially brilliant and exhibited kathodo-luminescence of an intense yellow color. They were also excited to some extent by X-rays, the CdSO$_4$ again showing the greatest intensity. In all cases the phosphorescence excited by X-rays was too small to be measured with the present apparatus.

The curves given in Fig. 119 show the change in the decay of willemite after heating. Curve *L* shows the decay of the untreated willemite. Curve *M* shows the decay after heating the willemite for 45 minutes at a

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[1] See Chapters IV and V.

bright red heat. It is clear from the curves that the heat treatment has decreased the initial intensity and made the decay less rapid; both these changes may be observed by the eye alone if the two screens are excited in a dark room. Willemite No. 3 which had been heated 2 hours was found to give a curve whose points fell so nearly on curve *M* that it was not plotted.

The effect of heat upon the decay in $ZnCl_2+xMnSO_4$ is similarly shown in Fig. 120. Curve *H* represents the decay in a sample of the substance taken as a dry powder, which was prepared by heating the mixture only 2 hours at a bright red. Curve *K* represents the decay of a sample heated 5 hours, and curve *G* after 7 hours heating. The curves show that the first heating was not sufficient to bring out the initial brightness and longer decay of the substance, and that there is a time limit to the heating necessary to produce maximum intensity; for on heating beyond this the initial intensity becomes less. From the behavior of this artificial compound it would seem that the natural willemite shown in Fig. 119 had reached a maximum heat treatment already, for further heating decreased its initial intensity. The slope of the curves in Fig. 120 indicate little change in the rate of decay after the initial drop; unfortunately the intensity becomes so small that it was found impossible to carry the curves farther. The readings in this region represent the average of a number of settings.

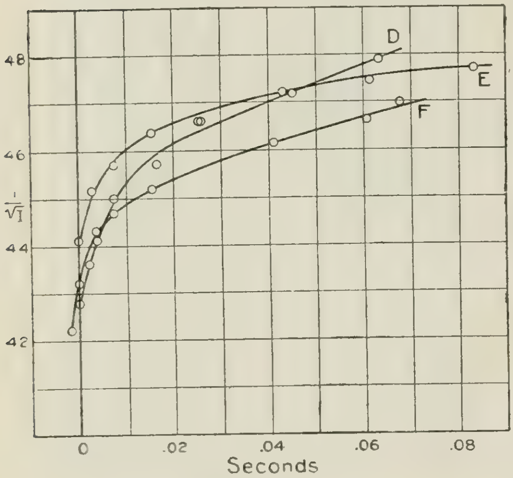

Fig. 118.

Showing the decay in different substances.
Curve *D*, CaS, time of excitation 0.033 sec.
E, $CdSO_4$, " " " 0.032
F, $CdCl_2$, " " " 0.031

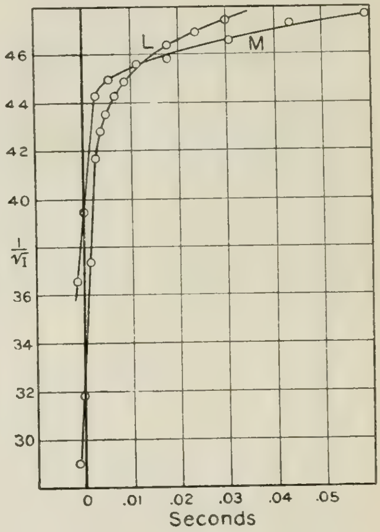

Fig. 119.

Showing effect of the heat treatment.
Curve *L*, willemite No. 1, time of excitation 0.022 sec.
Curve *M*, willemite No. 2, time of excitation 0.022 sec.

The curves given in Fig. 121 show the effect of changing the time of excitation in $ZnCl_2$ No. 3. This was accomplished by making the opening of the disk in Fig. 116 smaller. It was found that when the 60-cycle current was used for the spark the curves taken with decreased time of excitation were more or less irregular. This was no doubt due to the fact that with the small opening of the disk the irregularities of the spark were more pronounced. However, on the 140-cycle current the curves were quite regular and could be duplicated very closely. The curves given in Fig. 121 were taken with the spark operated from the 140-cycle current. It will be noted that a decrease in the time of excitation brings about a more rapid decay.

The curves in Fig. 121 also serve to confirm the results obtained with the 60-cycle current; for it will be seen that they have the same general shape as those given for $ZnCl_2$ No. 3 in Fig. 117.

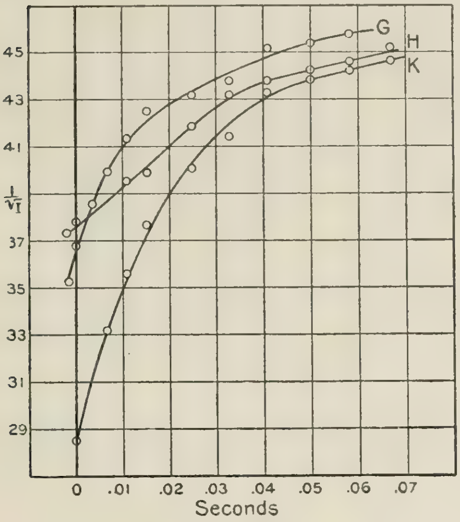

Fig. 120.

Curves showing effect of heat treatment.

Curve *H*, $ZnCl_2$ No. 1, time of excitation 0.031 sec.
K, " " 2, " " " 0.031 sec.
G, " " 3, " " " 0.031 sec.

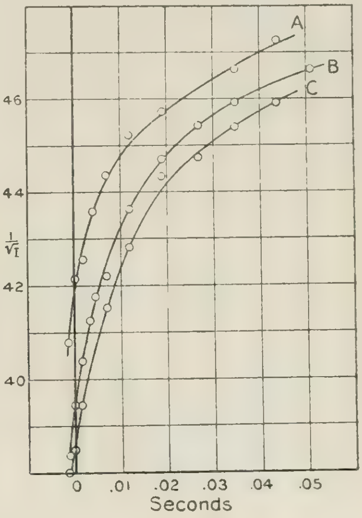

Fig. 121.

Showing the effect of changing the time of excitation.

Curve *A*, $ZnCl_2$ No. 3, time of excitation 0.013 sec.
B, " " " " " 0.024 sec.
C, " " " " " 0.058 sec.

EFFECT OF INFRA-RED ON THE INITIAL DECAY OF SIDOT BLENDE.

The effect of infra-red on long-time phosphorescence is well known,[1] and it was natural to expect that short-time phosphorescence would be affected in somewhat the same way. The method of experimentation followed was to allow the light from the arc to fall on the phosphorescent screen through a piece of very dense ruby glass, and to compare the shape of the decay curves taken with and without the infra-red. It was found, however, that none of the short-time substances were affected in measurable amount. There was a slight indication of some change in the shape of the later portion of the decay curve, but the error in setting the spectrophotometer in this region, where the light is so faint, would account for the observed change.

While the effect of infra-red on the decay of short-time phosphorescent compounds is so small that it can not be readily measured, the effect of infra-red on Sidot blende is well marked.

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[1] See Chapter V of this treatise.

In Fig. 122, curve *B*, showing the decay under the action of the infra-red, is the average of a number of determinations and the shape of the curve is fairly definite. The data for curve *A* are, however, less reliable. There is some doubt also as to the shape of the curve during the first hundredth of a second. It was necessary to change the position of the disk on the shaft of the phosphoroscope in studying the effect of infra-red and it is possible that the zero given may be incorrect, *i. e.*, the points on the zero ordinate and perhaps the one following may be in the fluorescent light, and therefore the real phosphorescent decay may have started at some later time than the zero given. This possible error in the zero only applies to the curves taken in studying the infra-red and in no way affects the other curves.

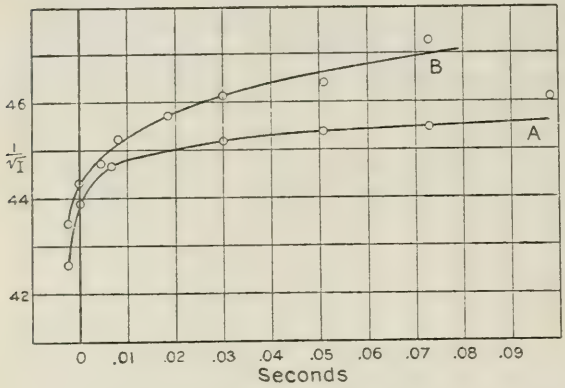

Fig. 122.

Curves showing effect of infra-red on initial decay of Sidot blende.
Curve *A*, without infra-red, time of excitation 0.04 second.
Curve *B*, with infra-red, time of excitation 0.04 second.

There is no question as to the effect of infra-red on the initial decay of Sidot blende, but owing to the very slow decay the shape of the curves may be more or less in error.

DECAY CURVES FOR DIFFERENT WAVE-LENGTHS.

In this determination the curves of decay were taken for different wave-lengths of the phosphorescence spectrum of several substances. So far as could be seen with the spectroscope all these spectra, at room temperature, consisted of a single band, the location and extent of which in each case is indicated in Table 18.

Table 18.

CaS	0.53	to	0.64 μ	with max. at	0.575μ
CdCl$_2$	.545	“	.65 μ	“ “ “	.59 μ
CdSO$_4$	.514	“	.623μ	“ “ “	.565μ
ZnCl$_2$ No. 1	.49	“	.585μ	“ “ “	.52 μ
Andrews' ZnCl$_2$	.49	“	.545μ	“ “ “	.52 μ
Willemite No. 1	.46	“	.56 μ	“ “ “	.52 μ

To determine the rate of decay of different parts of the band for any substance, two methods were used. One was to take a number of decay curves at different wave-lengths of the band, and to plot a curve showing the intensity, at a fixed time after excitation, for the different wave-lengths. In the second method the mirror of the phosphoroscope was fixed so as to reflect the light from the screen a certain time after excitation; then, by shifting the telescope of the spectrophotometer, the intensity of the phosphorescence was determined for the different wave-lengths. The phosphoroscope was then adjusted to give the decay at a later period, and the intensity for different wave-lengths was measured in the same way. Both of these methods gave the same results, *i.e.*, that all portions of the band seemed to decay at the same rate. The curves shown in Fig. 123 are typical for all the substances studied. In none of the substances was there an indication of a shift of the maximum of the curve as the decay went on. If any change occurs during the decay it is too small to be detected by the method used.

SPECTROPHOTOMETRIC STUDY OF THE CADMIUM-SODIUM COMPOUNDS.

The time of decay of these substances is so much longer than that of the others considered in this chapter that the phosphoroscope already described was not well suited to their study. A new instrument was therefore devised for the purpose. This machine is a modification of the phosphoroscope described by Kester,[1] but is so constructed that it is possible to determine curves of decay without changing the time of excitation.

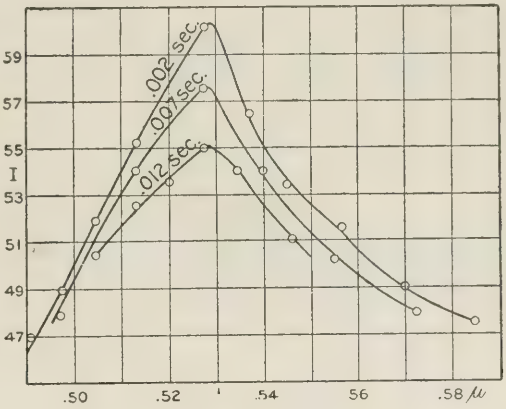

Fig. 123.

Curve showing the phosphorescence spectrum of $ZnCl_2$ No. 1, at different times after the exciting light was removed.

Fig. 124 shows the top view of the apparatus for making the decay curves. *W* is an iron pulley 45 cm. in diameter mounted on a vertical shaft. The mass of the pulley being considerable, it acted as a balance wheel on the driving motor to keep the speed constant. The speed was automatically recorded on a chronograph. The compound to be studied was sifted lightly over a strip of paper covered with "zapon" varnish; the strip of paper was then placed on the rim of the pulley. The spark gap *S* was mounted in such a way that it could be moved to different points on the periphery of the wheel without in the least disturbing the speed of the wheel or the continuity of the spark. This made it possible to maintain a constant excitation and still obtain the intensity of the phosphorescence at various times after excitation. The phosphorescent light to be studied enters the Lummer-Brodhun spectrophotometer at C_2. The comparison source is shown at C_1, and the telescope at *T*.

Fig. 125 shows the phosphorescence spectrum of a cadmium-sodium-manganate preparation taken with the apparatus just described and with an incandescent lamp as the comparison source.

Fig. 126 shows the phosphorescence spectrum of a cadmium-manganese-chloride compound. The distribution of intensities in these two cases is very similar and the spectra correspond closely with that of cadmium-

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[1] Kester: Physical Review, XXII, p. 280.

manganese-sulphate preparation previously observed, which showed a band extending from 0.514 to 0.623 μ, with a maximum at 0.565 μ. It would seem from these results that the manganese salts produce, when added to a cadmium salt, a phosphorescent compound whose spectrum shows the same maximum, and is independent of the salt.

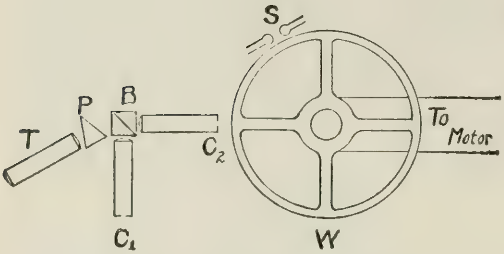

Fig. 124.

Showing top view of phosphoroscope.

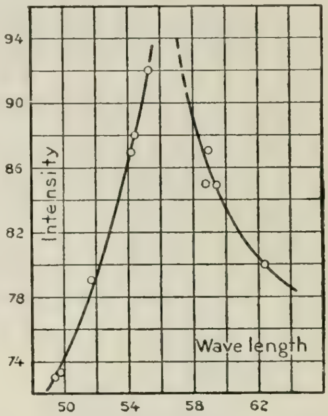

Fig. 126.

Showing the phosphorescence spectrum of a $CdSO_4$-$MnCl_2$ compound, taken 1.44 seconds after excitation.

Of the sodium salts this is not true, for the colors are widely different. An attempt was made to measure the spectrum of all the sodium compounds, but in most cases the intensity was far too small to measure.

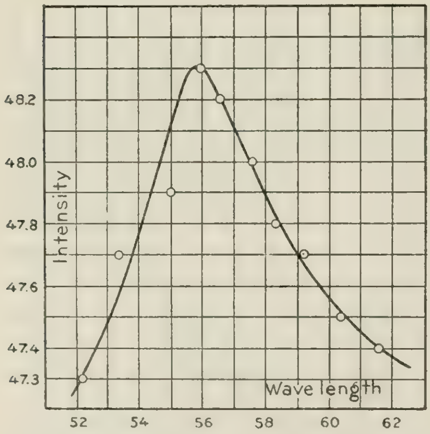

Fig. 125.

Showing the phosphorescence spectrum of a Cd-Na_2-MnO_4 compound, taken 0.374 second after excitation.

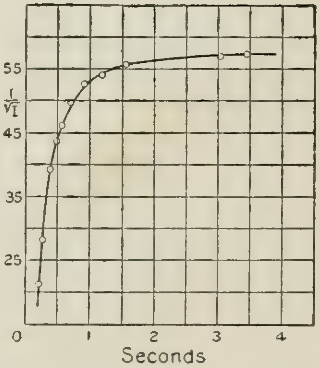

Fig. 127.

Showing curve of decay of a $CdSO_4$-NaBr compound.

Decay curves were taken from all the compounds whose intensity was sufficient to measure. All these curves show the same characteristics when plotted with the reciprocal of the square root of the intensity as ordinates and time in seconds as abscissas. Fig. 127, which gives the decay curve for cadmium sulphate with sodium bromide, and exhibits the two straight lines merging into each other, is a typical example.

SUMMARY.

The most important points brought out by the experiments here described may be briefly stated as follows:

1. The decay curve when plotted with the values of $I^{-\frac{1}{2}}$ as ordinates and corresponding values of t as abscissas consists of two straight lines gradually merging into each other. In this respect the short-time and long-time phosphorescent compounds seem to be similar.
2. The transition from fluorescence to phosphorescence is gradual, *i. e.*, the curve shows no sign of discontinuity.
3. The shape of the decay curve and the intensity depend upon the time of excitation.
4. The effect of heat treatment is such as to change both the intensity and the rate of decay of phosphorescence.
5. The effect of infra-red on short-time phosphorescence, if it exists at all, is very slight; but its effect on the initial decay of Sidot blende is quite marked.
6. The experiments indicate that at ordinary temperatures all portions of the phosphorescence band decay at the same rate.

THE EXPERIMENTS OF MR. CARL ZELLER.[1]

The experiments described below deal with the phosphorescence of three groups of compounds, namely, (1) the aniline dyes in their solid form; (2) a group of manganese compounds of known percentage concentration and a group of cadmium compounds, both prepared by C. W. Waggoner; (3) a group of four phosphorescent sulphides furnished by Leppin and Masche, and prepared by the method of Lenard and Klatt.

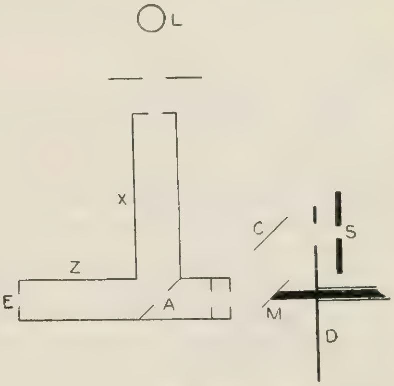

Fig. 128.

The phosphoroscope described on page 109 was used in connection with a special form of photometer, the arrangement of which is indicated in Fig. 128.

In the diagram *D* is the revolving disk of the phosphoroscope, *S* the spark gap, *C* the phosphorescent substance, *M* the revolving mirror. The photometer was made of two brass tubes *Z* and *X* set at right angles, with a mirror *A* mounted at 45° at the point of intersection of their axes. The mirror was a piece of microscopic slide glass cut in the form of an oval with a hole in the center and then silvered. This, when viewed from *E*, gave a contrast field with a patch of phosphorescent light in the middle surrounded by a disk of light

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[1] Carl A. Zeller, Physical Review, xxxi, p. 367.

reflected from the comparison lamp *L*. The color match was obtained by using screens consisting of films stained with various aniline dyes on glass. The lamp *L* was mounted on a photometer bar and could be moved through a considerable range of distances.

THE ANILINE DYES.

The aniline dyes were dissolved in either zapon, gelatin, water glass, or collodion, and flowed on glass. The glass proved to be too phosphorescent for its use; even oxidized brass emitted some light. Finally black broad-cloth was used as a background, and the samples were tested in powdered form, the phosphoroscope running at 2200 R.P.M. From a lot of fifty samples obtained from Heller and Merz, the following show both fluorescence (*F*) and phosphorescence (*P*) in slight degree: Naphthyl carmine, white; *F* blue, *P* very slight. Naphthyl sodium disulphonate, gray; *F* blue, *P* slight. Phthalic anhydride, white; *F* light blue, *P* slight. Naphthol sodium disulphonate, gray; *F* blue, *P* slight. Naphthol sodium monsulphonate, gray; *F* blue, *P* slight. Naphthol sodium sulphonate, gray; *F* blue, *P* trace. Beta-naphthol, white; *F* light blue, *P* trace. Tetrachlor phthalic anhydride, white; *F* blue, *P* slight. Alpha naphthylamine; *F* violet, *P* slight. Nitro-naphthylamine, light yellow; *F* green, *P* slight. Sulphonate of soda, reddish; *F* blue, *P* slight. Several of these show marked fluorescence when dissolved. Eosin, fluorescein, and rhodamin, in powdered form, show no trace of phosphorescence.

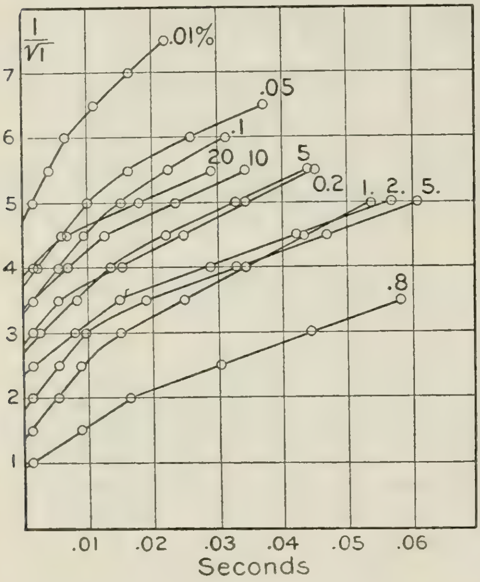

Fig. 129.

Manganese-chloride group, ranging from 0.01 to 20 percentage concentration.

THE MANGANESE CHLORIDE GROUP $NaCl\text{-}MnCl_2$.

The substances had been prepared by Dr. Waggoner by mixing solutions of $MgCl_2$ and NaCl in known proportions and evaporating to dryness. The percentage of $MnCl_2$ varied in different cases from 0.01 per cent to 2.0 per cent.

The samples were placed on brown cardboard with zapon varnish. The phosphoroscope ran at 600 revolutions per minute, or one revolution in 0.1 second. Time of excitation 0.025 second. The zero point was determined by readings taken at the point where reflected white light just disappeared. In making a reading the mirror was turned just far enough to shut off the direct reflected light. The standard was then moved until a definite match was obtained. The rest of the readings were made by moving the standard lamp one division and turning the mirror away from the zero point. The dimness of the phosphorescent light and the limit of the machine allowed but seven or eight points at most. The data plotted are the averages of three or four readings. The phosphorescence of this group is a pinkish red. In Fig. 129 the curves are plotted with time of decay as abscissas and $1/\sqrt{I}$ as ordinates, $1/\sqrt{I}$ being proportional to the distance of the standard lamp from the photometer screen. The lower and upper parts of the curves are straight lines, becoming concave downward as they approach each other. Several of the curves happen to have points taken at the bend and would indicate two straight lines meeting. All of the curves plotted with $I^{-\frac{1}{2}}$ as abscissas show the upper and lower parts as straight lines, gradually merging into one another.

The curves are in fact of exactly the same type as the decay curves obtained with Sidot blende.[1] A glance at the curves in Fig. 129 shows a marked tendency toward parallelism in both parts. According to the assumption of Wiedemann and Schmidt, that the light is emitted during the recombination of the products of the dissociation produced during excitation, this would indicate the same coefficient of recombination of the ions for the lower parts of these curves, and also the same, but slower rate in the upper parts. In this group the compounds that have the greatest initial intensity have the longest period of decay, although there seems to be no relation between the initial intensity and the time of decay. The cadmium compounds (Fig. 131) show just the opposite relation. The different slant in the two parts of the curves indicates a different coefficient of recombination and a different rate of decay for the two parts. The coefficient and the decay are smaller in the second part, showing a much slower process in the giving back of the stored energy.

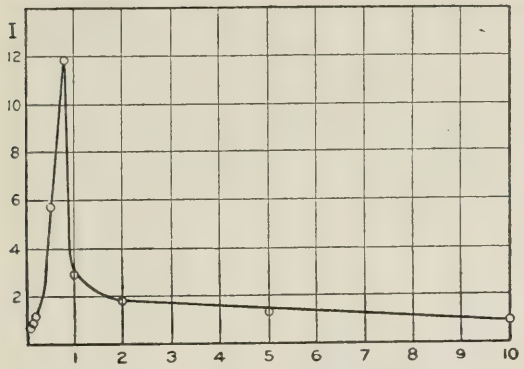

Fig. 130.

Showing relation between intensity and percentage concentration.

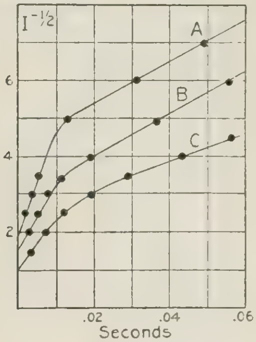

Fig. 131.

Decay curves for three cadmium compounds. The color of phosphorescence is green in each case. Time of excitation = 0.025 sec. *A*, $CdSO_4 + MnSO_4$ — phosphorescence; *B*, $CdSO_4 + MnCl$; *C*, $CdSO_4 + MnCl$ — different percentage.

The greatest intensity was shown by the compound of 0.8 per cent concentration. The relation between percentage concentration and initial

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[1] See Chapter V.

intensity is shown in Fig. 130 by plotting percentage concentrations as abscissas and initial intensities as ordinates. The initial intensities were obtained by extending the straight line of the first part of the curves in Fig. 129 to the *y* axis and reading the *y* intercept from the scale.

THE CADMIUM GROUP.

The phosphorescence of the cadmium compounds is yellow-green. Fig. 131 shows the decay curves for three different compounds. These are characteristic decay curves, and follow the general form. The compounds $CdSO_4+NaCO_3$, $CdSO_4+NaClO_3$, $CdSO_4+NaCl$, $CdSO_4+NaNO_3$, and $CdSO_4+NaBr$ were too dim to measure, but when excited may be seen in a dark room for several minutes. In this group the specimens that have the most intense phosphorescence have the most rapid decay.

SUBSTANCES OF SLOW DECAY.

A number of phosphorescent sulphides, made by the method of Lenard and Klatt,[1] were obtained from Leppin and Masche, Berlin. They consist of a sulphide, an active metal, and a flux. Practically all long-time and short-time decay curves have shown two distinct processes, merging into one. By this method it was possible, using long-time specimens, to study the first part of the first process, for the very first interval of decay. The specimens were excited for 0.008 second and the first readings made 0.0014 second after excitation. The curves shown in Fig. 132, plotted with time as abscissas and $I^{-\frac{1}{2}}$ as ordinates, are in all cases straight throughout the range studied. These results, which are in agreement with the results of Waggoner for Sidot blende, make it appear quite improbable that the behavior of the phosphorescent sulphides during the early stages of decay can be represented by an exponential law, as has recently been predicted by Lenard.[2] It should be pointed out, however, that the slant of the straight lines in Fig. 132 is such as to indicate an initial rate of decay far greater than that corresponding to what is usually called the "first process," or "Momentan-prozess," in the decay of substances of this class. It is possible that under the conditions of these experiments the decay curves of the phosphorescent sulphides consist of three portions, each of which is linear, or nearly so, when $I^{-\frac{1}{2}}$ is plotted against time.

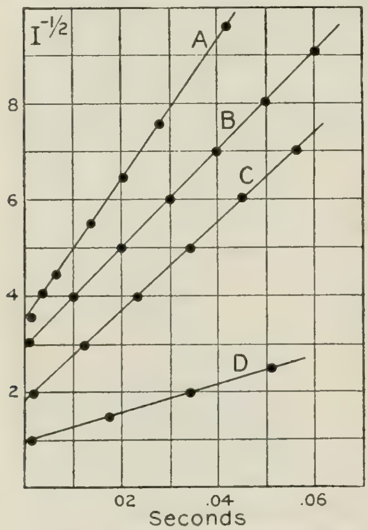

Fig. 132.

A, Sr-Bi-Na phosphorescence, green; *B*, Sr-Zn-F phosphorescence, green; *C*, Ca-Bi-Na phosphorescence, violet; *D*, Ba-Cu-Li phosphorescence, orange-red.

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[1] See Kayser, Handbuch der Spectroscopie, vol. 4, p. 750.

[2] Lenard Annalen der Physik, XXI, p. 641, 1910.

CHAPTER VIII.

PHOTOGRAPHIC STUDIES OF LUMINESCENCE.

Dr. C. A. Pierce, whose investigations of thermo-luminescence have been described in Chapter VI, has attacked by a photographic method some of the problems which arise in the study of the relations of fluorescence and phosphorescence and in the consideration of the form of the curve of decay. An account of his method and a summary of his results, which have an important bearing upon these questions, are given in the present chapter.[1]

THE DISTRIBUTION OF ENERGY IN THE FLUORESCENCE SPECTRUM AND THE PHOSPHORESCENCE SPECTRUM OF SIDOT BLENDE.

The method used in the study of the distribution of energy in fluorescence spectra consisted of photographing on the same plate the spectrum of the excited substance[2] and four spectra of an acetylene flame. Different intensities of the light from this flame were used for the four spectra, but the times of exposure of all four and of the fluorescence spectrum were the same. Knowing the distribution of energy in the acetylene flame,[3] the distribution in the fluorescence light was obtained by photometric comparisons of the spectra on the plate.

During the set of experiments the fluorescent powder was contained in a square dish made of platinum foil. The foil was connected to and supported by copper leads, so that the temperature of the powder could be raised and controlled by passing electric current through the foil. The temperature was measured, if different from room temperature, by means of a copper-constantan thermo-couple placed in the midst of the powder. The blue lines of a mercury-arc lamp were used to excite the powder. The various intensities of acetylene light were obtained by screening off all but the center of an acetylene flame and moving the flame with the screen to different distances from the slab of magnesia which reflected the light into the slit of the spectrum camera. The camera consisted of a direct-vision spectroscope set so that the spectrum could be focused on a sensitive plate held in a plate holder.

The plates were handled and developed in complete darkness. The developer was freshly mixed from a stock solution and of a standard strength, and the length of development was timed, being for most of the plates 8 minutes. The temperature was brought to 20° at the beginning of development and the plates were rocked mechanically during the development. The plates were fixed, at first for 30 minutes, after washing in three separate waters, and the temperature of the fixing bath was brought

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[1] See C. A. Pierce, Physical Review, XXX, p. 663; XXXII, p. 115.

[2] The substance employed was the "Emanations-pulver" used in the experiments described in Chapter IV.

[3] On the distribution of energy in the visible spectrum, by E. L. Nichols; Physical Review, XXI, p. 147, Sept. 1905.

to 20° at the beginning of the fixing. Later not so much care was used in the fixing because it was found to be inadvisable to intercompare spectra on different plates. After fixing, the plates were washed in running water for about 30 minutes, then thoroughly rubbed by hand and dried. Each plate was dried in such a position that the last portion to drain was a part upon which no measurements were to be made.

The distribution of denseness in any spectrum on a plate was obtained by pushing the plate past a brightly illuminated slit placed squarely across the spectrum, and measuring the transmitted light by means of a Lummer-Brodhun photometer. The source of light to illuminate the slit and the standard light consisted of two carbon-filament electric lamps with frosted bulbs. The light back of the plate was concentrated on the slit by a reflector. The current supplied to the lamps was held practically constant. It was found by actual test that a change of 5 volts was necessary to vary the relative intensities of the lamps enough to affect the settings of the photometer appreciably. The lamps were run at 6 per cent above normal voltage to increase the candlepower and were lighted only long enough to make the measurements.

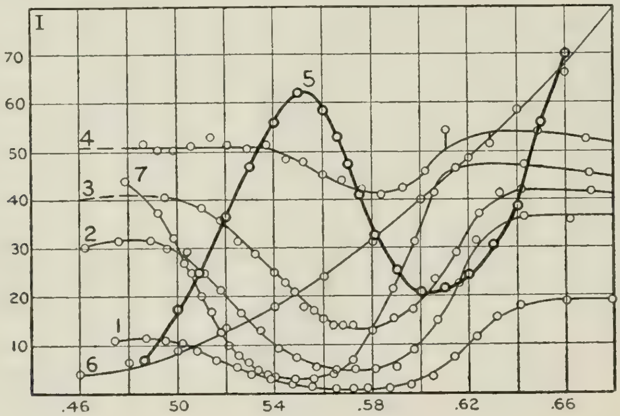

Fig. 133.

The wave-length measurements were made by calibrating in wave-lengths the screw which pushed the plate past the slit on the photometer bar. A zero wave-length was obtained on the plate by photographing the three blue lines of the mercury arc superimposed on the different spectra. These lines were in an entirely different region from that occupied by the spectrum of the fluorescence light. The calibration of the screw was made by photographing the entire visible spectrum of the mercury arc with the spectrum camera and setting one line after the other directly in front of the slit on the photometer bar. This slit was always opened just as wide as the width of the lines in the spectra and was placed parallel to these lines. The standard lamp was screened off by means of a variable slit, so that the photometer could be used on whatever part of the bar was desired.

Fig. 133 shows the curves obtained by plotting the light transmitted through the spectra on one of the plates which had been exposed as described above. Each exposure was 60 minutes long and was made with the slit opened 40 units. Curves 1, 2, 3, and 4 represent the spectra of acetylene light at intensities 32, 16, 8, and 4 respectively. Curve 7 represents the spectrum of the fluorescence light. Curve 6 represents the distribution of energy in the acetylene flame and is assumed to correspond to curve 3. Then the energy curve corresponding to curve 2 will have ordinates equal to 16/8 times the corresponding ordinates of curve 6, etc. Wherever curve 7 crosses curve 3, the energy for that wave-length is represented by the ordinate on curve 6 for that wave-length. Wherever curve 7 crosses curve 2, the energy for that wave-length is 16/8 times the ordinate of curve 6 for that wave-length, etc.

Since the curves intersect at only a few points, it was necessary to get other points on the desired energy curve by interpolation. This was done systematically and as follows: Suppose wave-length μ_1 is under consideration. A curve is plotted with the intensities of acetylene, 4, 8, 16, and 32, as abscissas and the intersections of the vertical at μ_1 with the curves 1, 2, 3, and 4 as ordinates. From this curve is picked off the intensity of acetylene that would have coincided with curve 7 at wave-length μ_1. Fig. 134 shows six curves drawn in connection with Fig. 133. Curves 1, 2, 3, 4, 5, and 6 correspond to wave-lengths $\mu=0.50$, 0.51, 0.52, 0.53, 0.54, and 0.55 respectively. The circle on each curve shows the point picked off. On curve 6, Fig. 134, 23.5 is the abscissa corresponding to 2.8, the ordinate on curve 7, Fig. 133, at $\mu=0.55$. Hence the ordinate at $\mu=0.55$ on curve 5, Fig. 133, which shows the distribution of energy of the fluorescence light is equal to $\frac{23.5}{8}$ times 21.3, the ordinate on curve 6, Fig. 133, at $\mu=0.55$.

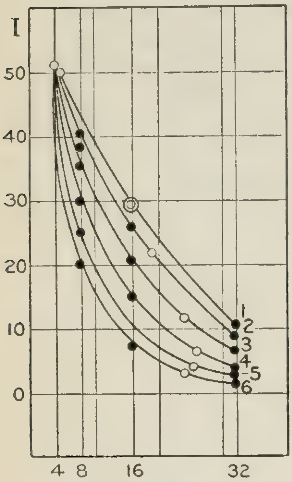

Fig. 134.

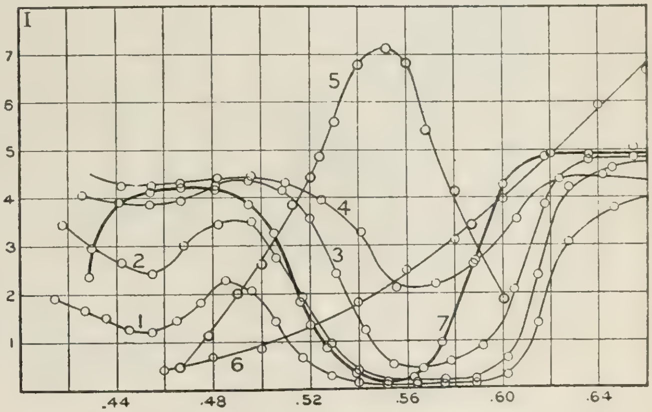

Fig. 135.

Curve 5, Fig. 133, shows the energy curve of fluorescence as computed from the other curves in Fig. 133. The curve has a well-defined maximum at $\mu=0.55$ and a minimum at $\mu=0.60$. The shape of the curve for wave-lengths greater than $\mu=0.60$ is uncertain.

Fig. 135 shows another set of curves corresponding to those in Fig. 133. The length of exposure was 30 minutes for each spectrum with a slit width of 20 units. The intensities of the acetylene flame were 32, 20, 12, and 6 for curves 1, 2, 3, and 4 respectively. Curve 6 is assumed to represent the energy distribution in curve 4. Curve 5, which shows the distribution of energy in the fluorescence light, is similar to the corresponding curve 5 in Fig. 133. This shows that the curve is not materially influenced by two factors, length of exposure and width of slit in the spectroscope.

The Sidot blende was excited by three blue lines of the mercury-arc spectrum. While these lines are in a different region of the spectrum from that occupied by the fluorescence band, yet there was considerable halation shown on the plates about the three lines and it was thought that this might extend far enough to change the shape of the curves in the region of smaller wave-lengths.

To test this matter a slab of magnesium carbonate was substituted for the Sidot blende and was illuminated in the same manner by the blue and violet lines of the mercury arc.

A plate was exposed to the light reflected from this slab and also, as in the previous experiments, to four different intensities of acetylene light. Curves showing the amount of transmitted light are given in Fig. 136.

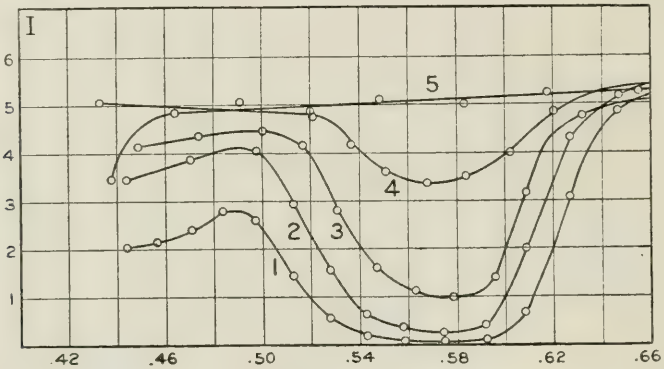

Fig. 136.

In this as in the previous figures curves 1, 2, 3, and 4 are for the acetylene light. Curve 5 indicates the transmission of that part of the plate exposed to the light of the mercury arc reflected by the magnesium carbonate. Since there is no indication of any effect it appears that halation from the mercury lines is inappreciable for wave-lengths longer than 0.46 μ and that no error from this source occurs in the curves marked 5 in Figs. 133 and 135.

Experiments were also made with very intense negatives in an endeavor to obtain the shape of the energy curves for wave-lengths greater than 0.60 μ, but on account of an apparent tendency to reversal in such negatives it was not found possible by this method to extend observations to these longer waves.

PHOSPHORESCENCE AT ROOM TEMPERATURE.

In order to obtain the distribution of energy in the phosphorescence light, it was necessary to add to the apparatus already described a shutter which would close the spectrum camera and excite the powder; then shut off the exciting light and open the camera. The shutter was operated by a constant-speed motor. Levers, springs, and triggers were so arranged that the shutter operated in a small part of a second. The length of excitation and decay could be increased or decreased together by changing the speed of the motor, while either the length of excitation or the length of decay could be varied alone by rearrangement of parts of the controlling devices. The total time of exposure of the photographic plate to the phosphorescence light was made equal to the length of exposure of the acetylene spectra.

With the apparatus described above, the photographic negative of phosphorescence was obtained by light which varied in intensity, for the phosphorescence decayed after the exciting light was closed off in the manner characteristic of phosphorescent powders. However, if an energy curve is obtained similar to that for fluorescence, it seems reasonably certain not only that the energy curve does not change with decay, but also that it does not change when the exciting light is shut off.

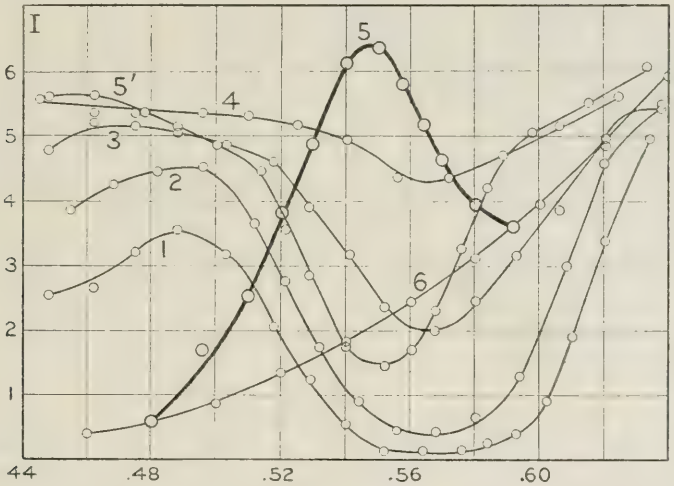

Fig. 137.

Fig. 137 shows the energy distribution in the phosphorescence light of Sidot blende. The powder was excited each time for 8.75 seconds and allowed to decay 10.33 seconds. The powder was not exposed to infra-red before each excitation. The effective length of exposure of the photographic plate was 60 minutes. Curves 1, 2, 3, and 4 show the transmitted light of the photographic spectra corresponding to intensities of acetylene equal to 6, 4, 2, and 1, respectively. Curve 5′ shows the transmitted light of the phosphorescence spectrum. Curve 5 shows the energy curve for the phosphorescence light.

It is seen that curve 5 is similar in form to the corresponding curves for fluorescence. The phosphorescence spectrum, at least in the early stages of decay, is thus the same as the fluorescence spectrum.

DISCUSSION OF METHOD.

The chemical change made in a photographic plate depends upon the wave-length and intensity of the incident light and upon the length of exposure. If several spectra are photographed upon the same plate and the length of exposure is the same for all the spectra, then the denseness of the different negatives at any wave-length will depend only upon the intensity of the incident light at that wave-length, assuming a small opening of the slit to the spectroscope, uniform development, non-halation, etc. Since intensity is proportional to the rate at which energy is received from the source, the denseness of the different negatives at any wave-length depends upon the energy received from the source at that wave-length. By making several negatives of one source of light of known energy distribution at different distances from the spectroscope, curves can be drawn showing the relation between energy received at any wave-length and denseness of negative. If a spectrum of another light of unknown energy distribution is photographed on the same plate, its energy distribution can be obtained by comparison of the denseness of its negative with the calibrated densities. The densities can be compared by means of the light transmitted through the negatives at different wave-lengths.

If the slit opening in the spectroscope is not very small, the denseness of the negative at any wave-length will not depend alone upon the energy received at that wave-length, but will also depend upon the energy received at wave-lengths differing but little from the wave-length in question. Consequently a small dimple in a curve might be obliterated by a wide slit opening. The effect of slit opening can be tested by using different openings, finally using the one which experience shows to be best.

The effect of halation is more troublesome than slit opening, and was present more or less in all of the negatives. The effect of halation is to broaden the band of energy distribution, but not to change the position of the maximum point of the band. It is believed that halation in the present experiments was not of sufficient effect to cause any serious error in the curves.

The plates were developed immediately after the exposures, which were made one directly after the other, so that any error due to continued chemical action after exposure in the film was eliminated as far as possible.

The photometric measurements were difficult to make because of the large differences in the amount of light transmitted in different parts of the negatives. At the beginning of the experiments, four settings of the photometer were made for each point measured. Later two settings were found to be sufficient, one approaching uniformity of illumination from each direction. The average of the two values calculated from the two settings was taken as the true ratio of standard and transmitted lights. Remeasurement of a set of curves never proved any exceptional accuracy, but always gave the same type of energy curve with the maximum at nearly the same wave-length. Consequently the measurements can be said to be substantially correct.

These experiments show that the energy curve of the fluorescence light of Sidot blende consists of a band extending from about $\mu=0.46$ to $\mu=0.60$, having a maximum at $\mu=0.55$. There may be another band situated in the region of longer wave-lengths. Furthermore, the energy distribution in the fluorescence light and the phosphorescence light immediately after excitation is the same.

THE PHOSPHORESCENCE SPECTRUM DURING DECAY AND THE QUESTION OF TWO OVERLAPPING BANDS.

In Chapters IV, V, VI, and VII of this memoir, the characteristic form of the curve of decay of phosphorescence for various substances and under a variety of conditions has been given and it has been shown to consist of two straight lines of different slopes which gradually merge into one another. In Chapter VI it was shown, moreover, that Becquerel's[1] expression for the decay could be made to fit the actual curves by assuming the existence of two overlapping bands having very different rates of decay.[2]

In Chapter IV measurements on the phosphorescence of Sidot blende were described and it was shown that in the case of Sidot blende the spectrum did not change its form during the first few seconds of decay.[3] A similar result was obtained by Waggoner[4] (see Chapter VII) for several other substances exhibiting phosphorescence of short duration.

While the presence of overlapping bands of differing duration would necessarily cause a gradual change in the distribution of intensities in the phosphorescence spectrum as decay progressed, these measurements were not decisive, as against the hypothesis of the existence of such bands. It was found in the case of the Sidot blende that the "first process" of decay lasted about 10 seconds, whereas the spectrophotometric measurements covered only 3 or 4 seconds. Dr. Waggoner's determinations likewise apply chiefly to the earlier stages of decay.

The experiments now to be described were undertaken to provide further data bearing upon the two-band theory of phosphorescence decay. The two rectilinear parts of the typical decay curve differ widely in slope. Hence, on the assumption of two bands, most of the light before the bend in the curve is due to the band corresponding to the steeper straight line (see Fig. 79, Chapter VI). At the bend the light is due more or less equally to both bands; and after the bend the light is due mostly to the second band. With a method available for studying the light distribution before and after the bend, the two-band explanation would be proved or disproved, depending on whether a change was or was not found in the distribution of the light.

As was shown in the first part of this chapter, the fluorescence spectrum of the substance used consisted of one prominent, symmetrical, smooth-sided band with a maximum at about $\mu=0.55$ (see Fig. 133). The band extends, approximately, from $\mu=0.46$ to $\mu=0.60$. Furthermore, the energy distribution immediately after excitation (Fig. 137) is the same as in the fluorescence spectrum.

The present work is concerned with the light distribution before and after the bend in the decay curve.

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[1] H. Becquerel, Comptes Rendus, 113, p. 618, 1891.

[2] See Chapter VI; also C. A. Pierce, Physical Review, XXVI, p. 312.

[3] See also Nichols and Merritt, Physical Review, XXI, p. 247.

[4] C. W. Waggoner, Physical Review, XXVII, p. 220.

EXPERIMENTAL.

The method employed to photograph the decaying band of phosphorescence was based on the assumption that the conditions and phenomena could be reproduced indefinitely, a fact already established for the substance under investigation. The phosphorescent powder, except in the case of Fig. 140, which gives the results obtained with Balmain's paint, was zinc sulphide, *i. e.*, the sample of "Emanations-pulver" used in the investigations described in Chapter VI.

The apparatus was that described on pages 130 and 131, but electrically operated shutters were used to excite the powder, to expose the plate, and to kill off the remaining phosphorescence with infra radiations before repeating the excitation. With this apparatus the decay curve could be photographed between any two points, time and time again, until an impression had been made on the photographic plate. Since, at best, the necessary exposure was very long, varying from a few hours to a much longer time, no attempt was made to deduce the energy distribution, but the photographic spectra were compared with each other, the principal weight being attached to the position of the maximum of the band. Care was taken to obtain negatives of about the same average density, and of not too great density, so that no complications could result from widely different or complete chemical change of the films at any wave-length. With these precautions, negatives were obtained which showed definite maxima, and the results could be repeated as many times as desired.

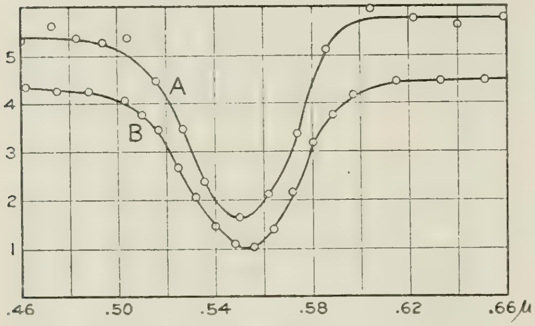

Fig. 138.

The distribution of denseness on the photographic film was measured, at first, with a photometer, as in the previous experiments; but this method was soon abandoned because of the eye strain induced by comparing very faint fields of light. The apparatus which was substituted consisted of a brightly illuminated slit placed before a very sensitive system of thermo-couples. The photographic plate was pushed past the slit by means of a screw calibrated in wave-lengths. Since the deflection of the galvanometer, which measured the current from the thermo-couples, depended upon the length of time that light was allowed to pass through the slit, a pendulum was made to light and extinguish the electric lamp which illuminated the slit, at predetermined intervals. With this apparatus results were obtained which were consistent with those obtained with the photometer, and the results could be repeated.

Fig. 138 shows the data obtained by measuring a film with the photometer (curve *A*) and with the thermo-couple (curve *B*). In this and in all subsequent figures ordinates represent intensities of transmitted light. These two curves are consistent as regards general shape and the position of the points of minimum transmission. Since intensities of transmitted light are plotted, the minima of the curves correspond to the maxima of intensities of the spectra. Inspection will show that curve *B* is not the exact duplicate of curve *A*; the ratios of the ordinates at long wave-lengths are not the same as at shorter wave-lengths. This lack of similarity did not exist in many of the comparisons and was, quite likely, due either to eye fatigue or else to the gradual warming up of the plate under successive exposures to the light which illuminated the slit.

Fig. 139 shows three curves corresponding to the decay of phosphorescence. In curve *A*, the Sidot blende was excited for 9.75 seconds and the plate was exposed for 8.25 seconds immediately after excitation. The powder was exposed for about 1 minute to infra-red rays and the process was repeated over and over until a sufficient exposure had been secured. In curve *B* the powder was excited for 21 seconds, allowed to decay for 14 seconds, then the plate was exposed for 15 seconds. In curve *B* the x-axis is raised so that curve *B* does not intersect curve *A*. In curve *C* the excitation was 5.5 minutes, the decay 1.5 minutes, and the plate was then exposed for 1 minute. The total time of exposure to produce the negative from which curve *C* was made was 72 hours. The negative was faint and the film was somewhat fogged, but remeasurements on the film always gave approximately the same curve. In fact, curve *C* is the average of several remeasurements. The minima of these curves occur at wave-length $\mu = 0.555 \pm 0.003$.

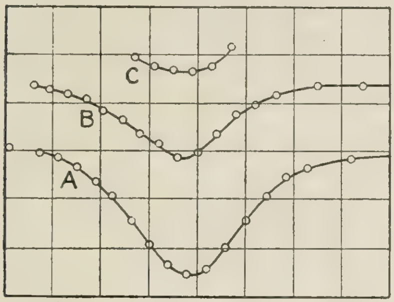

Fig. 139.

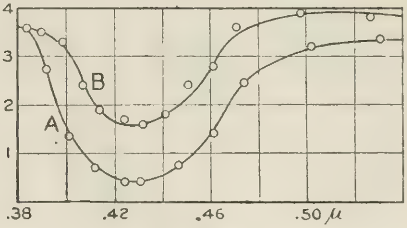

Fig. 140.

The bend in the curve of decay of the phosphorescence of Sidot blende occurs between 10 and 20 seconds after the end of excitation and is more pronounced the longer the excitation. Hence curve *A* in Fig. 139 is due chiefly to the light corresponding to the decay before the bend, while curve *B* corresponds to conditions near the bend, and curve *C* corresponds to conditions far beyond the bend. Or, in terms of the two-band theory, curve *A* corresponds mainly to band 1; curve *B*, to bands 1 and 2; and curve *C* to band 2 almost entirely. This set of curves shows no change in the maxima of the spectra, and indeed no set was obtained which showed any appreciable change.

The powder from which Balmain's paint is made, as will be seen by reference to Chapter IV, shows a more pronounced bend in the decay curve than is the case with Sidot blende. Two determinations were therefore made using this substance and showing the character of the spectrum before and after the bend. For each curve (see Fig. 140) the excitation was 5 minutes. For curve *A*, the plate was exposed 20 seconds immediately after excitation. For curve *B*, the phosphorescence was allowed to decay 1.5 minutes, then the plate was exposed for 1 minute. No shift in the minima of the curves can be detected, while a decided change in the shape of the curves would be expected if the two-band theory is correct.

A PHOTOGRAPHIC TEST OF THE EFFECT OF INFRA-RED RAYS.

The effect of infra-red radiations in suppressing phosphorescence and fluorescence has been considered at length in Chapter V, in which experiments were described indicating that all parts of a fluorescence band are suppressed in the same ratio. As a check on that work and because, on the assumption of the existence of two bands, one band would in all probability be suppressed more than the other, several runs were made in which the fluorescence spectrum of Sidot blende under the influence of infra-red rays was photographed. These rays were obtained from a 16 c.p. lamp held 5 cm. from the powder. The visible rays were screened off by means of thin rubber.

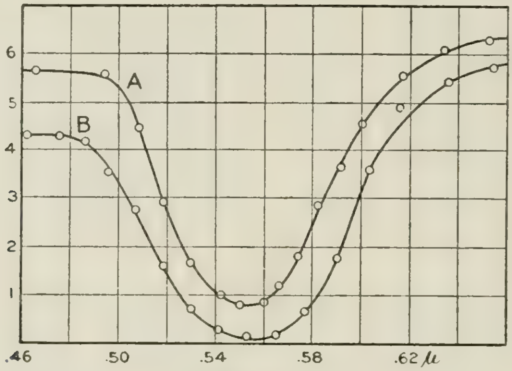

Fig. 141.

In Fig. 141 curve *A* corresponds to the fluorescence spectrum without infra-red excitation, and curve *B* with infra-red. The exposure of the plate in the latter was twice as long as in the former case. It will be seen that the minimum is not changed appreciably from $\mu = 0.555$ by the exposure to infra-red and that the curves agree very well in form, except at short wave-lengths.

In Fig. 142, curve *A* corresponds to the fluorescence spectrum without infra-red; curve *B* to the same with infra-red; and curve *C* corresponds to the phosphorescence spectrum just after excitation and is added for ease of comparison. In each case the minimum of the curve occurs at $\mu = 0.555$ approximately.

The effect of infra-red excitation on the fluorescence spectrum, according to all of the curves obtained, is to decrease the intensity of the band; but there is no change in the distribution of intensities that can be detected by this method and no measurable shift of the maximum. This result is in accordance with those recorded in Chapter V and it does not confirm the two-band theory of decay.

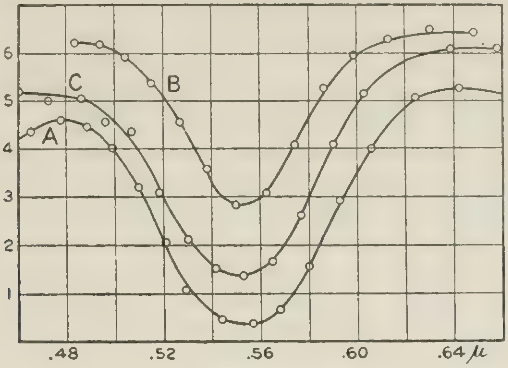

Fig. 142.

THE EFFECT OF TEMPERATURE ON THE FLUORESCENCE SPECTRUM.

It has recently been shown[1] that remarkable changes in the apparent complexity of fluorescence spectra are in some cases produced by changes in the temperature of the substance.

To determine whether such changes as could be detected by the present method take place in the fluorescence band of Sidot blende when that substance is excited at different temperatures a series of photographs were taken, the results of which are shown in Fig. 143.

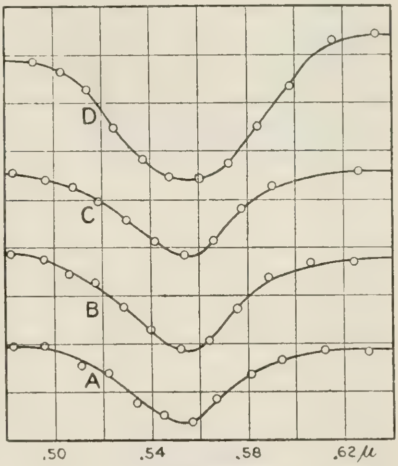

Fig. 143.

This figure contains four curves corresponding to the fluorescence of Sidot blende at different temperatures. In each case the length of excitation was varied so as to give, approximately, negatives of equal density, hence the dimming of the band at higher temperatures is not evident, though it occurred. In fact, the powder almost ceased to exhibit fluorescence when the temperature was raised sufficiently. When the temperature was lowered the powder would again show the same spectrum as before, provided a certain critical temperature had not been exceeded. The x-axis is changed for each curve, so that the points may be entirely distinct from one another. Curves A, B, C, and D were obtained at temperatures 22°, 67°, 88°, and 120° respectively. No shifting of the minimum can be seen.

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[1] Nichols and Merritt; Physical Review, XXXII, p. 38.

DISCUSSION OF RESULTS.

The accuracy of individual measurements with a non-direct method, such as the photographic method described in this chapter, is not great. Conclusions must be drawn from the indications of many experiments, rather than from the too exact interpretation of a single determination. A general survey of the curves obtained, of which only few examples have been given, shows that the minima, corresponding to the maxima of the usual curves of distribution previously employed, occur within the limits $\lambda = 0.555\,\mu \pm 0.003$. These limits were seldom exceeded and the variations were not consistent with each other. For some sets of curves the limits could be contracted to $\pm 0.002\,\mu$ or possibly to $\pm 0.001\,\mu$. Hence, if the maximum of the band changed under any of the conditions, it must have been within the limit $\pm 0.003\,\mu$ and probably within even smaller limits. From certain considerations, such as the bend in the decay curve of phosphorescence, and the smooth, symmetrical shape of the whole band, one would expect, if the two-band theory is correct, a considerable change in the band under the conditions studied. No changes were found that were not explained by the limitations of the method.

Hence the following conclusions are drawn from the work above:

1. The fluorescence and phosphorescence bands of Sidot blende coincide with each other.

2. No change in the position of the band of phosphorescence occurs with decay in the case of either Sidot-blende or Balmain's paint.

3. No change in the position of the band of fluorescence occurs under the action of infra-red rays.

4. No change in the position of the band of fluorescence occurs with a change, between +20° and +120°, in the temperature of the powder.

5. No change in the shape of the band, discernible by this method, was found under any of the above conditions.

CHAPTER IX.

A SPECTROPHOTOMETRIC STUDY OF CERTAIN CASES OF KATHODO-LUMINESCENCE.[1]

The spectrophotometric study of luminescence has thus far been confined almost entirely to cases of photo-luminescence. It is of interest to inquire whether exciting agents other than light will give luminescence spectra of the same type, and to what extent the laws that have been found to hold in the case of photo-luminescence possess a more general application. The experiments on kathodo-luminescence described in the present chapter are of interest chiefly because of the bearing of the results upon these and similar questions. During the course of the work preliminary data have also been obtained with regard to the dependence of kathodo-luminescence upon discharge potential and current strength.

The form of the vacuum tube used is shown in Fig. 144, the substance to be tested being placed at *S*. In order to prevent disturbance from the fluorescence of the glass the specimen in some instances was placed in a metal inclosure which protected the glass from excitation by the kathode rays. The kathode, *K*, was a flat aluminum disk. The fluorescent light was reflected directly into the slit of the Lummer-Brodhun spectrophotometer by a small mirror at the side of the tube. An acetylene flame was used as a comparison source. Current was furnished by a motor-driven Holtz machine capable of giving a current of 0.6 milliampere. A galvanometer placed in the circuit next to the grounded pole of the machine served to indicate the constancy, or lack of constancy, of the current through the tube. In most cases relative values only of the current have been recorded. The potential difference between the terminals of the tube was measured by a Kelvin electrostatic voltmeter and served as a sensitive indicator of changes in the vacuum.[2]

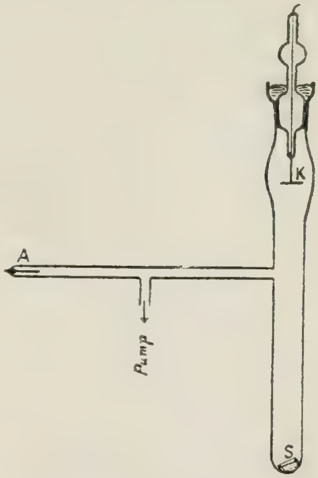

Fig. 144.

Considerable difficulty was encountered in keeping the discharge through the tube steady. Sudden changes occurred in the intensity of the fluores-

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[1] The results contained in this chapter were in part presented to the American Physical Society, at the meeting held in Washington, April 24, 1908, and were published in the Physical Review, XXVIII, p. 349.

[2] Since the absolute values of the potential used are of no great significance in the present work, we have plotted voltmeter readings rather than the actual values of the potential in the curves contained in this chapter. If the potential in volts is desired this may be found by multiplying the voltmeter deflection by 385.

cence, even without any corresponding change in current or voltage, due apparently to some erratic cause producing either a deflection of the kathode rays or a change in the intensity of these rays. The most serious of these disturbances were traced to irregular leakage from the wires leading to the Holtz machine. This trouble was made more difficult to control by unfavorable atmospheric conditions, the work being carried on in the spring; but the disturbances due to leakage were largely removed by using large rods in place of wires, and by avoiding sharp corners. It proved advantageous, also, to run the Holtz machine at full speed and to cut down the potential difference between the terminals of the tube by means of resistance in series. The necessary resistance was furnished by a tube containing absolute alcohol. Flickering persisted to some extent even with these precautions, and it was frequently necessary to discard the results of several hours work. The results given here were, however, taken under favorable conditions.[1]

It did not prove practicable to maintain the pressure in the tube constant during the time necessary for spectrophotometric measurements throughout the spectrum. Owing to a small leak, or to the development of gas by the discharge, the pressure gradually increased during the course of a series of readings, so that at the end of about an hour it was necessary to reexhaust. In order to determine the luminescence spectrum corresponding to constant pressure conditions the following procedure was adopted:

While one observer recorded the readings of the voltmeter and galvanometer and, when necessary, operated the pump, the other made settings of the spectrophotometer as rapidly as possible, running back and forth through the spectrum until the whole region had been covered a number of times. Curves were then drawn for each wave-length at which settings had been made by plotting intensities, as measured by the spectrophotometer, against voltmeter readings. A series of such curves is shown at the left in Fig. 145, which refers to a cadmium sulphate preparation. These curves all have the same general shape, and in most cases each curve contains enough points to determine its form with considerable definiteness. After the curves had been drawn as accurately as possible the intensity corresponding to any particular voltmeter reading could be determined by graphical interpolation. The points which form the two curves to the right in Fig. 145 (marked I. V. M. 30 and II. V. M. 17.5) were determined in this way for the voltmeter readings 30 and 17.5 respectively. For these curves the abscissas are wave-lengths expressed in fractions of μ as indicated.

The procedure in the case of our experiments with willemite (Fig. 146) and Sidot blende (Fig. 147) was exactly the same as in the case of cadmium sulphate. A comparison of these three figures shows, however, that while the voltage intensity curves in Figs. 145 and 146 are similar, being in each case concave toward the horizontal axis, the corresponding curves in Fig. 148 are almost exactly straight. The difference results from the fact that in the experiments corresponding to Figs. 145 and 146 the current through the tube diminished rapidly as the voltage increased, whereas in the experi-

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[1] It is probable that the trouble was due to electrostatic charges on the walls of the tube. A larger tube so constructed as to have the kathode at a considerable distance from the walls would probably have been more satisfactory.

ments on Sidot blende (Fig. 148) the conditions as regards leakage were more favorable and the current remained nearly constant. During the observations corresponding to Fig. 148 the deflection of the galvanometer varied from 32 for the highest voltmeter reading (33.8) to 37 for the lowest voltmeter reading (11.7). In the experiments with willemite (Fig. 146) the galvanometer deflection ranged from 7 to 25; and in the experiments with cadmium sulphate the range was from 15 to 31.

The results obtained are plotted in Figs. 145 to 148 and are further discussed below.

$CdSO_4+xMnSO_4$.—This substance was prepared by C. W. Waggoner, who has determined its decay curve when excited by the iron spark.[1] Excited by kathode rays it gave an intense yellow fluorescence, with scarcely observable phosphorescence. Close inspection of the powder showed occasional grains which glowed with an orange or red light. At the end of our experiments, after the powder had been bombarded by the kathode rays for about 10 hours, the surface was found to have acquired a ruddy brown discoloration. Upon standing for several months the powder scarcely responded at all to excitation by the iron spark, but recovered its activity after heating.

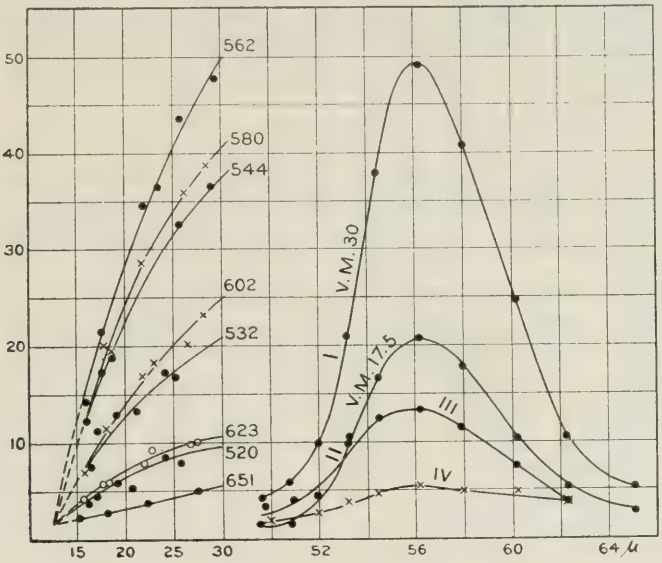

Fig. 145.

$CdSO_4+xMnSO_4$. The curves to the left show the relation between discharge potential and intensity for different wave-lengths. Curves *I* and *II* show the luminescence spectra for discharge potentials of 11,600 volts and 6,700 volts respectively. Curves *III* and *IV* show, to a larger scale, the luminescence spectra excited by ultra-violet light and Roentgen rays respectively.

Inspection of curves *I* and *II*, Fig. 145, shows that the form of the fluorescence spectrum is independent of the discharge potential, and therefore of the velocity of the kathode rays, since it is clear that one of these curves might be obtained from the other merely by changing the scale.

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[1] Waggoner, Physical Review, XXVII, p. 209, 1908. See also Chapter VII of this memoir.

The fluorescence spectrum was also determined for excitation by the ultra-violet rays in the spectrum of the iron spark, and for excitation by Roentgen rays, the results being shown in curves *III* and *IV*, respectively. The luminescence excited in both of these rays was weak and the spectrum could be explored only with great difficulty. Curves *III* and *IV* are drawn to a much larger scale than curves *I* and *II* in order that they may be shown in the same figure. In reality the intensity at the maximum of curve *I* is 200 times as great as the corresponding intensity for curve *III*, and 500 times as great as the maximum for curve *IV*. It will be observed that the maximum of curve *IV* occurs at the same wave-length as in the case of kathodo-luminescence. In the case of photo-luminescence, curve *III*, there is an apparent shift toward the shorter waves. We are of the opinion, however, that this shift is not real, but due to errors resulting from the extreme faintness of the spectrum.

The substance continued to glow for a long time when excited by ultra-violet light, but after excitation by kathode rays the phosphorescence died out with great rapidity.

WILLEMITE.

The specimen which was tested was a part of the same piece that had previously been used in determining the decay of phosphorescence in this substance.[1] No change was observable in the specimen, even after prolonged excitation.

While the kathodo-luminescence of willemite was not much more intense than that of $CdSO_4$, the photo-luminescence, excited as before by the ultra-violet rays from an iron spark, was found to be much brighter than that of $CdSO_4$. The luminescence excited by Roentgen rays was, however, only slightly more intense. Curves *IV* and *V*, Fig. 146, which show the spectral distribution for the photo-luminescence and the Roentgen luminescence respectively, are plotted to a larger scale than the curves for kathodo-luminescence on the same figure, as it would otherwise be impossible to see the details of these curves. The maximum intensity for curve *I* was in reality 120 times as great as that for curve *IV* and 1,500 times as great as for curve *V*.

Inspection of the curves of Fig. 146 seems to justify the conclusion that the luminescence spectrum of willemite has the same form whether the exciting agent is ultra-violet light, Roentgen rays, or kathode rays. The form of the spectrum is also seen to be independent of the potential difference between the terminals of the tube, and is therefore independent of the velocity of the kathode rays.

When excited by ultra-violet light the willemite used in these experiments showed bright phosphorescence, whose rate of decay was so slow as to be comparable with that of Sidot blende. But when excited by kathode rays the phosphorescence was faint and disappeared within a few seconds. The intense brilliancy of the kathodo-luminescence during excitation makes this difference especially striking.

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[1] Nichols and Merritt, Physical Review, XXIII, p. 37, 1906. See also Chapter IV of this memoir.

SIDOT BLENDE.

The specimens tested were pieces of the same screen that had been used in the work on Sidot blende described in Chapters IV and V.[1]

Our first measurements of the kathodo-luminescence of this substance were made in connection with this earlier work, and although the conditions were not so definite as in the case of the more recent investigation, the result of one exploration of the spectrum, shown in Fig. 147, will be of interest for purposes of comparison. Kathode rays were developed in these experiments by connecting the tube used with the secondary of an induction coil, the primary of which was supplied with alternating current. The discharge was made approximately unidirectional by placing a rectifying tube in series. The current was controlled by an alcohol resistance. The current used being smaller than that employed in our more recent work, less difficulty was met with in maintaining constant pressure in the tube. That the pressure was nearly constant during the measurements corresponding to Fig. 147 is shown by the fact that it was possible to run

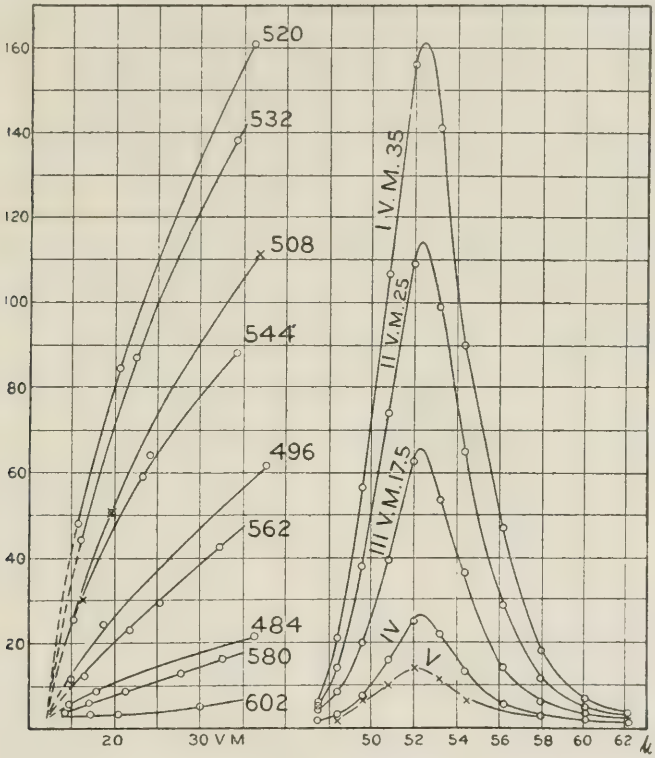

Fig. 146.—Willemite.

The curves to the left are voltage-intensity curves for different wave-lengths. Curves *I*, *II*, and *III* show the luminescence spectra for discharge potentials of 13,500 volts, 9,600 volts, and 6,700 volts respectively. Curves *IV* and *V* show, to a large scale, the luminescence spectra excited by ultra-violet light and Roentgen rays respectively.

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[1] Nichols and Merritt, Physical Review, XXI, p. 247; XXII, p. 279; XXIII, p. 37; XXV, p. 362.

through the spectrum a second time with practically identical results. The points marked by circles in Fig. 147 were determined first, while those marked with crosses were taken afterwards, with no change in the conditions, as a check. It is clear that the spectrum contains two overlapping bands, and the estimated curves for the separate bands are indicated by the dotted lines.

Our more recent measurements with Sidot blende were made by the same method as that used with $CdSO_4$ and willemite. The results are shown in Fig. 148.

When subjected to the relatively intense kathode rays used in these experiments the Sidot blende was found to undergo a rapid change, which was manifested both by a discoloration of the surface and by a diminution in the intensity of the luminescence. In Fig. 148, curve *III* corresponds to the same voltmeter reading as curve *I*, but was taken after the substance had been excited continuously for 2 or 3 hours. Not only is the intensity much diminished by prolonged excitation, but the whole character of the luminescence spectrum is altered.

The band at about 0.5 μ, which appears in Fig. 147 and in curves *I* and *II* of Fig. 148, appears to be the same as that excited by light and by Roentgen rays.[1] The band at about 0.455 μ, is also excited by Roentgen rays.[2] But this band is either not present in the spectrum excited by ultra-violet light, or is masked by the other bands present in that spectrum. The luminescence of Sidot blende, as we have previously pointed out, is extremely complex, and the green band at about 0.51 μ is the only one which can be readily isolated.

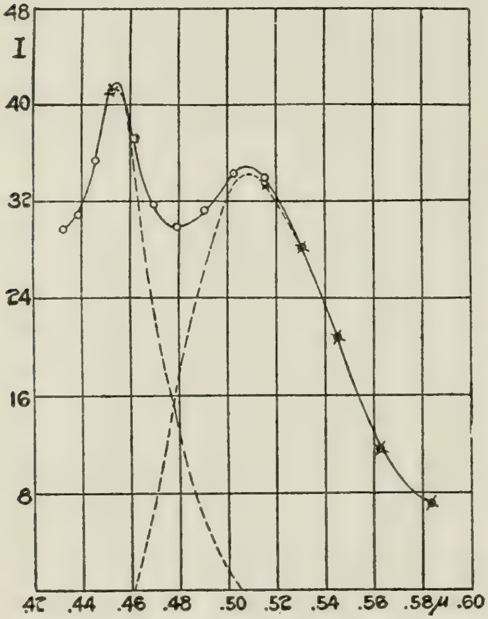

Fig. 147.—Sidot blende.

When excited by kathode rays the phosphorescence of Sidot blende is faint and of relatively short duration.

The infra-red rays obtained by interposing a thin sheet of hard rubber in the path of the rays from an arc diminished the kathodo-luminescence of Sidot blende only slightly. A long series of settings, alternately with and without infra-red rays, was necessary to make certain that any effect was produced at all. Infra-red rays of the same intensity would have cut down the fluorescence excited by light to one-half its normal intensity.[3]

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[1] Nichols and Merritt, Physical Review, xxi, p. 247, 1905, Figs. 30, 31, and 35. See also Chapter III, Fig. 40.
[2] See Fig. 41, p. 44.
[3] Physical Review, xxv, p. 362, 1907. See also Chapter V of this memoir.

DEPENDENCE OF KATHODO-LUMINESCENCE UPON CURRENT AND DISCHARGE POTENTIAL.

Since kathodo-luminescence results from the bombardment of the luminescent substance by the kathode rays it is natural to expect a simple relation between the intensity of luminescence and the velocity and number of the kathode-ray particles. The experiments here described show that the *form* of the luminescence spectrum is independent of both these factors. The experiments show also that the intensity of luminescence is increased by increasing either the velocity of the rays or the current in the tube. But the conditions of the experiments were unfortunately not such as to permit definite conclusions to be drawn regarding the quantitative relations.

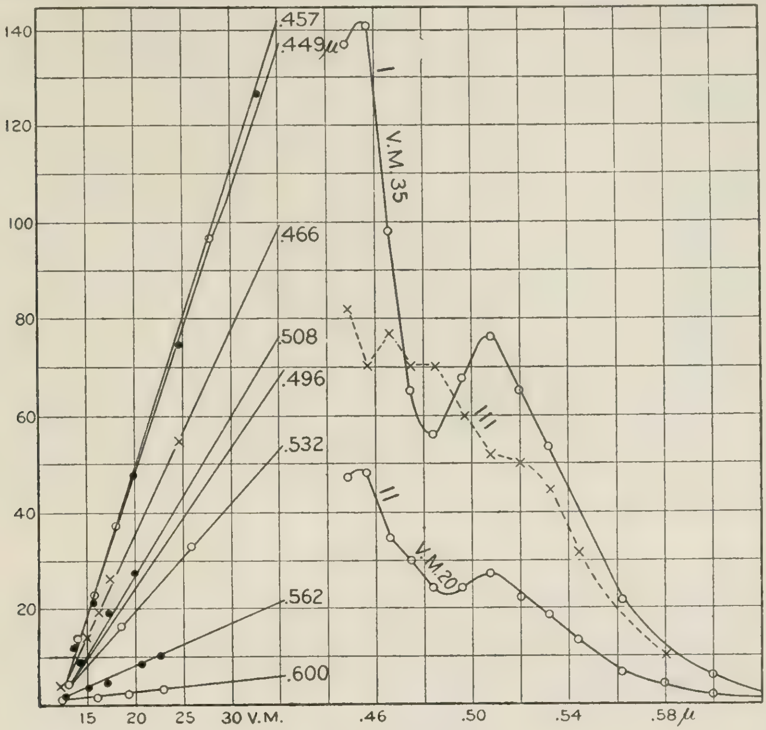

Fig. 148.—Sidot blende.

The curves to the left are voltage-intensity curves for different wave-lengths. Curves *I* and *II* show the luminescence spectra for discharge potentials of 11,600 volts and 7,700 volts respectively. Curve *III* shows the luminescence spectrum for 11,600 volts after the substance had been altered by the action of the kathode rays.

Several attempts were made to determine the relation between intensity and current at a constant discharge potential. The current could be varied through a wide range either by changing the speed of the Holtz machine or by altering a resistance in multiple with the tube. The results make it seem probable that the intensity of luminescence is proportional to the current; but erratic changes in the conditions in the tube, due probably to static charges on the walls, made it impossible to get entirely consistent results. For a time the conditions would apparently remain constant and the intensity was found to vary in the same ratio as the current. But some source of disturbance soon developed, so that the next observations were discordant. Some change in the form of tube or the source of current supply will be necessary before this question can be definitely settled.

Working with the relatively slow kathode rays developed by ultra-violet light, Lenard has found the intensity of luminescence, I, to be related to the discharge potential, V, by the equation

$$I = CQ(V - V_0)$$

where Q is the density of the kathode stream, C a constant, and V_0 a minimum potential below which no luminescence is produced.[1] The existence of a sharply defined lower limit to the potential that is capable of producing luminescence is called in question by Wehnelt,[2] who used in his experiments a much greater density of the kathode rays. On the other hand a definite lower limit to the velocity has been found by Rutherford[3] in the analogous case of luminescence produced by the α rays of radium.

Our own experiments with Sidot blende appear at first glance to confirm the conclusions of Lenard, for the voltage-intensity curves, Fig. 148, are straight lines cutting the horizontal axis at a point corresponding to a voltmeter reading of about 12 divisions. In the case of the experiments with Sidot blende the current in the tube varied only slightly. We are not justified in concluding, however, that the density of the kathode stream was constant, for the fraction of the current that is carried by the kathode rays is known to vary as the vacuum changes, being practically zero at high pressures and nearly 100 per cent when the pressure is low. In our experiments it was not practicable to determine the amount of this change. It seems scarcely probable, however, that the change was unimportant. If the curves of Fig. 148 could be corrected so as to refer to a constant density of the kathode stream it appears probable that they would differ greatly from the curves plotted.

CONCLUSIONS.

In so far as it is possible to generalize on the basis of the small number of experiments here described, the following conclusions appear to be justified:

1. In cases of kathodo-luminescence the distribution of intensity throughout each band of the luminescence spectrum is independent of the discharge potential, and therefore independent of the velocity of the kathode rays.

2. In cases where a band is capable of being excited by light and by Roentgen rays as well as by kathode rays, the form of the band and the position of its maximum are the same for all these modes of excitation.

We have shown in Chapters III and IV that the distribution of intensity in any given band is independent of the wave-length of the exciting light.[4] It appears probable, therefore, that the above conclusion may be stated more broadly, and that the distribution of intensity in each band of a luminescence spectrum is independent of the nature of the exciting agent by which the luminescence is produced.

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[1] Lenard, Annalen der Physik, 12, p. 449, 1903.
[2] Wehnelt, Berliner physikalische Gesellschaft, 5, p. 225, 1903.
[3] Rutherford, Radioactivity, second edition, p. 547.
[4] Nichols and Merritt, Physical Review, XVIII, p. 403; XIX, p. 18.

3. Phosphorescence following excitation by kathode rays is less intense and more fleeting than the phosphorescence excited in the same substance by light.

The explanation of this fact is probably to be found in the relatively slight penetrating power of the kathode rays. The excitation is thus confined to a thin layer at the surface of the active substance, while in the case of photo-luminescence the excitation extends to a considerable depth. As will be pointed out in Chapter XV of this memoir,[1] the decay of phosphorescence would be more gradual in the latter case.

4. The effect of infra-red rays upon kathodo-luminescence of Sidot blende during excitation is small compared to the same effect upon the photo-luminescence of this substance and produces a barely observable decrease in the intensity of luminescence.

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[1] Nichols and Merritt, Physical Review, XXVII, p. 373, 1908.

CHAPTER X.

ON THE ELECTRICAL PROPERTIES OF FLUORESCENT SOLUTIONS AND VAPORS.

THE INFLUENCE OF FLUORESCENCE UPON ELECTRICAL CONDUCTIVITY.

The effect of light and of Roentgen rays upon the conductivity of solutions has been tested by Cunningham,[1] in the case of five solutions, one of which, namely, uranyl nitrate, was fluorescent. In the experiments with light an arc containing iron was used as a source, and the solutions were contained in a cell having a quartz window, the object being to obtain intense ultraviolet rays. Although some indication of increased conductivity was observed, the observations were rendered so uncertain by the heating effect of the rays from the arc that the author did not regard the results as reliable.

Experiments of a similar character were undertaken by Regner[2] with especial precautions against the disturbances due to the heating effect of the source. No change in conductivity as great as 0.1 per cent could be detected, although the substances tested included those for which Cunningham had found indications of a positive result. Several fluorescent substances were tested by Regner, also with negative results.

In a paper by Burke[3] on the change in absorption due to fluorescence, mention is made of preliminary experiments upon the conductivity of fluorescent substances; but the author states that difficulties were met with which led him to abandon these experiments and to take up the study of absorbing power instead.

Our own experiments upon this subject were undertaken with the feeling that the increase in conductivity due to fluorescence was probably very small, comparable rather with the conducting power produced in gases by the action of Roentgen rays than with ordinary electrolytic conductivity in solutions. In attempting to detect so small an effect it seemed advisable to work with solutions in which the normal conducting power was as small as possible. In the case of all the substances thus far tested we have therefore used absolute alcohol as a solvent.[4]

The accurate measurement of the resistance of alcoholic solutions offers considerable difficulty; for while the conducting power is too great to permit the employment of an electrometer method, such as would be used with gases, it is too small to be determined with accuracy by the methods generally used with aqueous solutions. No benefit was to be gained in the present experiments by increasing the cross-section of the liquid tested, and so reducing its resistance; for if the thickness exceeded a rather small

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[1] J. A. Cunningham, "An attempt to detect the ionization of solutions by the action of light and Roentgen rays," Proc. Cambridge Philosophical Society, II, pp. 431-433. 1902.

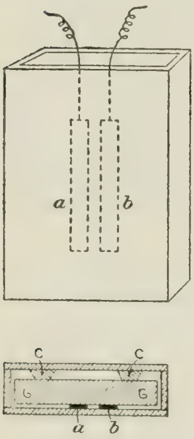
[2] Physikalische Zeitschrift, 4, 862, 1903.

[3] Burke, Philos. Transactions, 191A, p. 87.

[4] In the experiments of Cunningham and Regner the solvent was water.

value the absorption of the liquid made it impossible to excite the whole mass to fluorescence. After trying a number of different methods without satisfactory results we abandoned the attempt to accurately measure the total resistance, and directed our attention to the measurement of the *change* in resistance due to illumination. The most satisfactory method that we have found for this purpose is that of the ordinary Wheatstone bridge, using a direct current and a galvanometer of high resistance.

The form of the cell used to contain fluorescent solutions is of considerable importance in its bearing upon the sensitiveness of the method. Among the galvanometers available for use with the bridge, that which seemed best suited for the work was one having a resistance of about 10,000 ohms. It was therefore desirable to have the resistance to be tested as near to this value as other conditions would permit. On the other hand, the layer of liquid tested should be so thin that it can be excited to strong fluorescence throughout its thickness. Although we did not find it possible to satisfy both of these conditions, they were approximately met by the form of cell shown in diagram in Fig. 149.



SECTION

Fig. 149.

The figure shows both a perspective view and a horizontal section of the cell. A thick piece of plate-glass, *G*, was cut of such a size as nearly to fill the cell and was held in position, tightly pressed against the two electrodes *a*, *b* (of platinum foil), by the corks *C*, *C*. Although the drawing is in other respects approximately to scale and nearly actual size, the thickness of the electrodes *a*, *b* is greatly exaggerated. The thickness of the layer of liquid between *G* and the walls of the tube was determined by the thickness of the electrodes and was about 0.1 mm. In the section shown in Fig. 149 the portions occupied by the solution are left unshaded. The length of the electrodes was about 20 mm. and their distance apart 2 mm.

The fluorescent substances tested were eosin, fluorescein, rhodamin, napthalin roth, and cyanin. As already stated, the solvent was in all cases absolute alcohol. The solutions were made quite concentrated, so that fluorescence was confined to a thin layer at the surface. The concentration was so adjusted as to make this fluorescent layer approximately 0.1 mm. thick.

The cell containing the solution to be tested was made one arm (C) of a bridge. The resistance of the arm M in series with C was in all cases 9,000 ohms, while the resistance of the third arm, R, was 5,000 ohms. The fourth arm, N, was varied until an approximate balance was obtained[1] and the apparent resistance was computed by the formula $C=MR/N$. Current was furnished by two gravity cells in series.

Polarization in the fluorescent solution made it impossible to obtain the true resistance by this method, and the apparent resistance of the cell (computed as if polarization were absent) is doubtless in error by 50 per

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[1] These resistances were chosen not because they gave the highest attainable sensitiveness, but because they were the most suitable ones that were available at the time.

cent or more. But the sensitiveness of the arrangement to changes in the resistance of the test cell was high. In order to avoid disturbances due to variations in the polarization E.M.F. it was found necessary to keep both the battery circuit and the galvanometer circuit closed. Even the small change made in N during the adjustment of the balance produced a considerable alteration in the polarization, so that the adjustment often had to be continued for an hour or more before the needle of the galvanometer was sufficiently steady for observations to be begun. During this time the cell was protected from the action of light by an opaque screen. When the conditions had become steady, or more frequently when the motion of the galvanometer needle was reduced to a slow uniform drift, the screen was removed and light from an arc was allowed to fall on the cell. After the effect of illumination had been noted, and when the needle had again settled down to a steady drift, the screen was replaced, and the throw of the needle in the opposite direction was observed.

In the measurement of so small an effect as that here considered it is clear that the heating effect of the rays from an arc is likely to produce serious errors, for the change in conductivity due to rise in temperature is in the same direction as the change that we are attempting to detect. For this reason the use of the direct rays of the arc, even at the distance of a meter, was entirely out of the question. Even when a water cell was interposed in the path of the rays the needle was displaced through several hundred divisions. That this movement of the needle was due to rise in temperature, and not to the effect sought, was indicated by the fact that the change persisted after the rays were cut off; it was necessary to wait at least 15 minutes before the original balance was approximately restored.

In order to avoid the disturbances due to rise in temperature we dispersed the rays from the arc by a prism and used only those portions of the spectrum that were most effective in producing fluorescence. With this arrangement the effects observed were much smaller than before, but they were entirely free from any indication of temperature changes. Upon removing the screen, so as to illuminate that part of the fluorescent solution lying between the electrodes, a throw of the galvanometer needle was observed, and if originally free from drift the needle vibrated about a new position and finally came to rest. Continued illumination of the solution produced no increase in the deflection. Upon replacing the screen a throw in the opposite direction occurred, and the needle finally returned to its original reading. If observations were made while the needle was in motion, these throws were simply superposed upon the steady drift. In this case the effect of illumination was measured by the average of the two throws.

So far as we were able to judge, the effect produced by light reached its full value at once and ceased as soon as the light was cut off. The disturbance of the balance of the bridge was always such as to indicate an increase in the conductivity of the fluorescent solution. Upon repeating the experiments with rays from different portions of the spectrum it was found that a change in conductivity was produced only by those rays which were able to excite fluorescence in the solution tested. And so far as we could estimate the intensity of fluorescence by the eye, the rays which gave the most intense fluorescence also produced the greatest change in conductivity. In the case of eosin we were able to follow both effects to the extreme edge of the violet, while illumination by the red of the spectrum produced no effect.

In order to form an estimate of the magnitude of the change produced we observed in each case the throw caused by increasing or decreasing the resistance N by one ohm. By comparing this with the throw due to illumination, it was possible to express the observed change as a fraction of the normal (apparent) resistance. The results are given in Table 19. The light used to illuminate the solution, in the case of the measurements included in the table, was that which produced the brightest fluorescence.

We have also tested in the same way one solution that was not fluorescent, namely, an alcoholic solution of fuchsin. The result was entirely negative. No change in resistance due to illumination could be found in any part of the spectrum, although the sensitiveness of the bridge was such that a change of 0.008 per cent could have been detected. The solution was an old one and had probably been made with commercial alcohol, since the resistance, 90,000 ohms, was much lower than that of the other solutions. For this reason we are not inclined to look upon this single experiment with a non-fluorescent solution as possessing much significance.

TABLE 19.

Increase in electrical conductivity due to fluorescence.

Substance.	N	Apparent resistance of solution.	Throw produced by illumination.	Throw produced by increasing N by 1 ohm.	Increase in apparent conductivity due to illumination.
			mm.	*mm.*	*per ct.*
Eosin...........	155	300,000	57	33	1.1
Napthalinroth...	45	1,000,000	1	39	0.05
Fluorescein......	300	150,000	10	30	0.11
Rhodamin.......	360	125,000	20	40	0.14
Cyanin..........	170	270,000	40	45	0.52

In the preceding description of the experiments upon fluorescent solutions we have ascribed the observed movements of the galvanometer needle to a change in the *resistance* of the solution. The galvanometer deflections undoubtedly indicate a disturbance in the balance of the bridge; but this disturbance might equally well result from a diminution in the E.M.F. of polarization. Without special modifications the method does not permit a separation of these two effects. In the case of eosin, however, special experiments were made bearing upon this point.

The experiments referred to were of two kinds. In the first of these a bridge method was employed as before. The solution was contained in a glass tube originally about 5 mm. in diameter. A portion of this tube had been drawn down to a diameter of about 1 mm. and the current passed through the liquid contained in this contracted part. The platinum electrodes were placed in the larger part of the tube at each end. We were thus able (1) to illuminate the solution about either electrode while the remainder of the tube remained dark; or (2) to illuminate the contracted part of the tube while screening the electrodes. In the latter case the effect was observed, as in the experiments already described. In the former case only a very small change could be detected.

The other experiments with eosin that bear upon the question of polarization were of an entirely different character, and represent one of our many early attempts to devise a satisfactory method of attacking the general problem. Fig. 150 shows both the form of tube used to contain the solution and a diagram of the connections. The platinum-wire electrodes *a*, *b* were connected to the terminals of the secondary of an induction coil, *I*, and to the two pairs of quadrants of an electrometer, *E*. The electrode *C* at the center of the tube was connected to the needle. The primary of the induction coil was excited by an alternating current of 120 cycles. When the solution was not illuminated the electrometer needle stood nearly at its zero. Under these circumstances illumination of the upper half of the tube produced a deflection in one direction, while the illumination of the lower half gave an approximately equal deflection in the opposite direction. The direction of the deflection in each case was such as to indicate a decrease of resistance. The spectrum of the arc was used in these experiments as in those made by the bridge method; and the evidence that the effect was due to fluorescence, and not to rise of temperature, was as conclusive as in the experiments previously described. The method was less sensitive, however, and was therefore used only in the case of eosin.

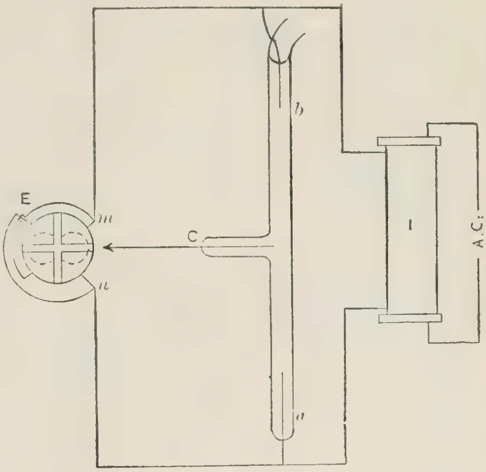

Fig. 150.

Shortly after the announcement of the results just described,[1] Camichel,[2] in a paper in the Journal de Physique, reported a series of measurements with entirely negative results, and suggested that our precautions against heating were insufficient and that the apparent change of conductivity might be thus explained. It seemed desirable, therefore, particularly as our experiments had been merely preliminary and prospective, to investigate further. Dr. Percy Hodge, at our suggestion, took the matter in hand and it was found, as will appear from the summary of his work given in the second part of this chapter and from a later paper by Goldman,[3] that the effects of light were much more complicated than had been suspected.

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[1] Nichols and Merritt, Physical Review, XIX, p. 415, 1904.
[2] Camichel, Journal de Physique, IV, 1905.
[3] Goldman, Annalen der Physik, VII, p. 322, 1908.

PHOTO-ACTIVE CELLS WITH FLUORESCENT ELECTROLYTES (DR. HODGE'S EXPERIMENTS).[1]

Before going on to any further systematic investigation, Dr. Hodge attempted to repeat as nearly as possible some of the experiments described in earlier portions of this chapter.

The substance first chosen for experiment was eosin, and nearly all the results to be described were obtained with this substance. As a solvent absolute alcohol was used, and in most cases the solution was saturated at room temperature.

The essentials of the apparatus used in these preliminary tests are shown in Fig. 151. The source of light *A* was a Schuckert arc lamp inclosed in the light-tight cover which is used with the lamp for projection. After passing through a pair of condensers the beam of light illuminated the slit *S*, then went to a water cell *W*, and thence to a lens and crown-glass prism, finally forming a spectrum on the front of the light-tight box *D*, containing the cell *C*. *D* was provided with a sliding front by which the light could be admitted to the cell *C*.

For measuring the change of resistance an ordinary Wheatstone bridge was used, the cell being placed in one arm. The source of current was a battery of gravity cells, the number of which was varied, as will be seen later. A very sensitive Sullivan d' Arsonval galvanometer of 1,100 ohms was used with the bridge. The galvanometer was fitted with a concave mirror of 4 feet focus, and its constant with the scale at that distance was 90×10^{-11} ampere per millimeter deflection.

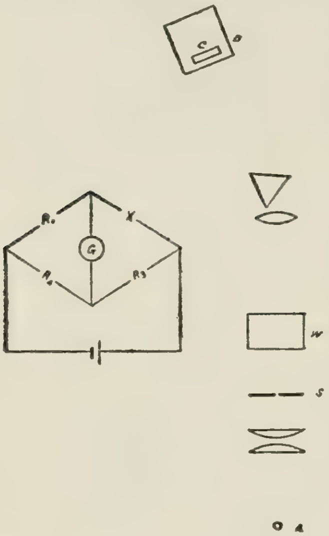

Fig. 151.

Fig. 152.

The cell used to contain the solution was a small rectangular glass cell 6 cm. deep and 1 cm. from front to back on the inside. In this were placed side by side, and at a distance of approximately a millimeter apart, two strips of platinum foil 0.1 mm. in thickness, 5 cm. long, and 3 mm. wide. Behind these in the cell was placed a piece of plate glass, holding the electrodes pressed against the front wall of the cell, and itself held in place by brass springs between it and the rear wall of the cell. A section of the cell is shown in Fig. 152, the thickness of the electrodes and other dimensions of the cell being considerably exaggerated. The dispersion of the prism gave a visible spectrum at the point where the cell was placed about 4 cm. wide. Thus the portion of the spectrum illuminating the narrow space 1 mm. wide between the electrodes was quite small, and it was easy to select the part of the spectrum producing maximum fluorescence without including the

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[1] This section is a summary of a paper by Dr. Percy Hodge; see Physical Review, XXVI, p. 540; and XXVIII, p. 25.

rays of longer wave-length which would be likely to produce heat disturbances. In the case of the eosin cell the light used was at the infra edge of the green.

When the cell was first set up great difficulty was experienced in obtaining a balance, the drift toward higher values of the resistance being quite rapid and continuing for several hours. This was at first thought to be due entirely to polarization, but it was found that if the top of the cell was covered so tightly that evaporation was prevented the drift lasted for only a short time, after which a comparatively steady condition was reached, and accurate measurements were possible. At no time was the cell absolutely free from a very slow drift, always toward higher resistance, and probably due partly to polarization and partly to a very gradual decomposition of the electrolyte. Evidence of the latter was seen in a very narrow strip of colorless liquid which was observed along the inner edge of the anode after several hours of application of the current. On account of this decomposition most of the tests were made with cells which had been freshly set up, the electrodes being removed and carefully cleaned between tests.

The method of the experiment was as follows. After the apparatus had been set up and the cell placed in its dark box the slide was raised and the cell so adjusted in the spectrum that the liquid between the electrodes became brilliantly fluorescent. The slide was then dropped, shutting off the light, and a balance was obtained with the bridge. The resistance of R_1 (see Fig. 151) was in nearly every case 10,000 ohms, that of R_3 was 50,000 ohms, and R_4 was adjusted to suit the resistance to be measured. As it was impossible to set the electrodes at exactly the same distance from each other when the cell was set up at various times the apparent resistances differed from each other greatly during different sets of readings. Also the polarization E.M.F. in the case of eosin was found to be over two volts. Therefore when two gravity cells were used the apparent resistance was much higher than when four were used.

After the cell had stood in darkness long enough to obtain a fairly steady condition of the bridge, the slide was suddenly removed and the cell illuminated.

With two volts as the applied E.M.F. the result was an immediate and very large decrease of resistance, the amount of resistance change required in the variable arm to restore a balance indicating as high as 10 or 15 per cent increase of conductivity. When the light was shut off the cell returned immediately to nearly the same resistance that it had before illumination. The test was repeated many times and on different days, and always with about the same results. As the effect was much larger than any that had been anticipated it seemed advisable to see if it could in any way be due to heating of the liquid. With this end in view the temperature coefficient of the solution was determined in the following manner: A balance was obtained at the temperature of the room. Then the cell was surrounded with ice water and a balance again obtained. Lastly the ice water was drawn off and the cell allowed to regain the temperature of the room. The first and last values of the apparent resistance were in turn subtracted from the second and then averaged. The result showed a temperature coefficient between zero and 20 degrees of not more than 1.5 per cent per degree. The effect of the light was also tried while the cell was in ice water and found to be apparently about as large as at room temperature. These tests seemed to preclude the possibility of any considerable portion of the effect being attributable to heat. An additional reason why the effect should not be attributed to heat was mentioned on page 149 of this chapter, namely, the fact that the change of conductivity took place within an exceedingly short time after the light was thrown on the cell, and after the light was shut off the cell immediately resumed its former state. This fact was confirmed in the course of these experiments, the time required for the change to take place being apparently considerably less than a second, and the decay of the effect taking about the same time.

A series of tests was then made with the same cell and solution, but using four gravity cells in series as the source of E.M.F. A difference of effect from that obtained with two cells was expected, as with two cells only a very small current could possibly have passed through the cell, since the applied E.M.F. was not equal to the E.M.F. of polarization, while with four volts the current flowing was of considerable magnitude. The effect anticipated was one similar to the first but of smaller magnitude. When the light was thrown on the cell, however, the surprising result was obtained of a large *increase* of resistance instead of a decrease as in the former experiments. The effects were produced as promptly as those of the preceding experiments and died away nearly as quickly.

Here was something quite unexpected. If the remarkable decrease of resistance observed in the first experiments was due to electrons set free by ionization of the solution accompanying the phenomenon of fluorescence it seemed highly improbable that an increase of resistance would be produced by light under any conditions whatever. Further, both effects were entirely too large to be satisfactorily accounted for by any theory analogous to that applied to the phenomena of ionization in gases; phenomena which it might be supposed would very probably accompany fluorescence.

Again, if the decrease of resistance in the first case were due to ionization of the nature of that produced in gases, it should be greater in dilute solutions than in concentrated, since, owing to the greater penetration of the light into a dilute solution the number of molecules affected would be as great as in a concentrated solution, while, owing to the greater distance between the molecules, the mean free path of the ions would be greater and therefore recombination less rapid. A number of experiments were made by diluting the saturated solution with two, four, and six parts by volume of alcohol, and the effects were found to be greatly diminished, so that even in the solution with two parts of alcohol there was a change of not more than 1 per cent in resistance.

In order to vary the conditions it was thought worth while to try next a cell in which, as in Regner's experiments, the liquid could be kept moving past the electrodes while being illuminated. All possible heat effects would be in this way eliminated, and some light might be thrown upon the nature of the phenomena which would not be brought out when the liquid was at rest. A cell was therefore prepared in the following manner, again copy the designing of one described on page 150.

A glass tube of 5 mm. internal diameter was drawn down at its middle point to a capillary about a millimeter in outside diameter and 1.5 cm. in length. Into the larger parts of the tube at each end were led platinum wires in the form of spirals to serve as electrodes. The upper end of the tube was attached to a tubulated bottle to serve as a reservoir for the liquid. To the lower end was attached a second capillary tube to hold the liquid back and keep the first capillary full. With this apparatus the liquid could be illuminated while flowing through the capillary at any rate desired. Numerous tests were made with the apparatus, and in all cases the results were entirely negative. The form of the cell was such, however, that its resistance was much larger than that of any of the cells previously tried, and as the sensitiveness of the bridge was much less under these conditions, the results were looked upon with some suspicion.

Another form of circulation cell was therefore devised which was free from the above objection.

A piece of glass tubing was obtained whose internal cross-section was almost that of a figure 8, except that where the two loops of the 8 would cross one another there was an opening between them about 0.3 mm. in width. In a short length of this tubing were placed two No. 16 platinum wires, each having a length of 5 cm. The wires were parallel to one another in the two loops of the 8, and from the end of each a small platinum wire was led out through the walls of the tube. There was thus left (see Fig. 153, which shows an enlarged cross-section of the cell) a narrow space between the electrodes through which the liquid could flow, the electrodes themselves almost filling the loops of the 8. Below the electrodes the tube was drawn down to a coarse capillary to make it possible to keep the space between the electrodes filled with liquid. The upper end of the tube was attached to a tubulated bottle as in the last experiment. By illuminating the contracted part of the tube between the electrodes a moving strip of liquid about 0.3 mm. wide and 0.1 mm. from front to back could be excited to fluorescence, while the current flow was from side to side of the strip at right angles to its length.

Fig. 153.

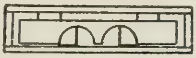

Fig. 154.

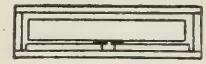

Fig. 155.

Upon connecting the cell to the bridge its resistance reached a steady value almost immediately after the current was turned on, and retained the same value as long as the motion of the liquid continued.

The movement of the liquid was quite rapid, the time required to empty the 400 c.c. reservoir being about 10 minutes. As the whole space between the electrodes held not more than 0.1 c.c. a complete change of liquid between the electrodes could not have occupied more than a fifth of a second.

Numerous tests were made with this apparatus, but in no case was there any evidence of a change of conductivity while the liquid was in motion. When, however, the lower end of the tube was stopped the effects reappeared, though they were not as marked as in the original type of cell. The sensibility of the bridge as used in these tests was at least 0.01 per cent. Therefore it seems fair to conclude that there could not have been any appreciable effect due to electrons set free at the instant fluorescence began in any part of the liquid, unless this effect required a considerable time to make itself known.

Attention was next given to the effects at the two electrodes separately and to the liquid between them, to find out, if possible, just where the phenomena took place which caused the changes in conductivity.

As nothing but negative results were to be obtained from a circulation cell the original type of cell was again adopted, and in the front of the box *D* of Fig. 151 was placed a screen with a vertical slit cut in it about 4 mm. wide. By placing the cell behind this screen in such a manner that only one electrode could be seen from the front of the box through the slit, it was possible to observe the effect of illuminating one electrode at a time, the other being in darkness behind the screen. With this arrangement and two gravity cells the effect was tried on anode and kathode in turn. When the anode was exposed the effect was very small, while on the contrary when the kathode was exposed the effect was found to be about as large as when both were exposed. As some of the liquid between the electrodes was illuminated in either case it was not certain whether the effect was produced only at the electrode or whether the liquid at a distance from the electrode also played its part in it. Therefore the question as to what would happen when the electrodes were both covered and the liquid between them exposed had next to be settled.

To this end several different arrangements of the cell were tried. The first tests were with the same electrodes which had been used in the earlier type of cell, but in front of each of them was placed a thin strip of hard rubber 0.15 mm. thick, projecting just beyond the platinum strip so as to completely screen it from the light, but so as to leave about 80 per cent of the liquid between the electrodes exposed to the light.

With this arrangement no effect could be obtained by illumination. However, it was felt that the test was not conclusive, for the total thickness of the film of liquid acting as conductor between the electrodes was that of both the electrode and the rubber strip, and since the absorption coefficient of a saturated solution of eosin is very large it was not at all certain that the whole thickness of the layer was illuminated.

To overcome this difficulty another type of cell was constructed after the following manner:

A block of hard rubber was sawed of such shape and size as nearly to fit the rectangular cell used in most of the experiments. The block was then clamped to a block of ebonite and with a $\frac{3}{8}$-inch drill two holes were bored between the blocks in such a manner as to leave in each block a pair of grooves of semicircular cross-section, and separated from each other by a narrow strip approximately 2 mm. wide. The block that had been sawed to fit the cell was then placed in the cell and two L-shaped electrodes were placed in the grooves in the positions shown in Fig. 155, which illustrates a section of the cell with block and electrodes in place. It will be seen from the figure that the electrodes hold the ebonite block back from the front wall of the cell, so as to leave a film of liquid of the thickness of the platinum strips between the two grooves when the cell is filled with liquid. The film of liquid between the grooves could be perfectly illuminated, was isolated from the electrodes, and at the same time included a large part of the total resistance.

Careful tests were made with this cell and the results were entirely negative, though the resistance of the cell was quite low compared with others that had been tried, averaging about 40,000 ohms with saturated solution, and the sensibility of the bridge was as high as 0.005 per cent. The conditions within a few minutes after it was set up were very steady indeed, and a slight change of conductivity would have been readily detected.

In addition to the saturated solution a solution of five parts alcohol to one of saturated eosin solution was tried with both 2 and 4 volts E. M. F., but likewise with entirely negative results. From the results of these last experiments it was evident that a change of conductivity in the liquid itself, except at or very near the electrodes, did not take place when fluorescence was produced.

It had frequently been observed that, however smooth the strips of platinum were when they were placed in the cell, and however tightly they were clamped against the front wall, when the solution was poured in a thin film of liquid immediately crept up between the electrodes and the front wall of the cell. There seemed, therefore, to be two regions in which the effects might be produced, either at the inner edges of the electrodes or in the region in front of the electrodes, or in both places at once.

From a variety of minor indications which had been noticed from time to time it seemed probable that the main effect was to be looked for in the thin film and not at the edges of the electrodes. In order to test the matter the effect was first tried of placing thin strips of ebonite in front of the electrodes as in one of the previous experiments, but instead of covering the electrodes the ebonite strips were only allowed to cover the extreme outer edges of the platinum strips, thus leaving nearly the whole of the electrodes exposed to the light, but behind a layer of liquid a number of times as thick as the capillary film formed when the electrodes were against the front wall of the cell. The change of conductivity, though still present, was found to be very greatly diminished.

As mentioned in connection with a previous experiment, the reduction of the effect might easily have been due to the absorption of the light by the thick layer of liquid in front of the electrodes, so that fluorescence did not occur at the surface of the platinum strips.

A second arrangement was then tried in which the platinum strips were separated from the front wall of the cell by strips of lantern-slide cover-glass a millimeter in thickness. The inner edge of each electrode (see Fig. 155) was allowed to project slightly beyond the edge of the glass. Thus the capillary film between the electrode and strip of cover-glass could be illuminated while the inner edge of the electrode was completely screened from the light by a thick layer of liquid. When the light was turned on this cell the effects were found to be present in as great a degree as when the whole of the electrode was illuminated.

Lastly, the platinum strips were again placed against the front wall of the cell and the inner edges covered, while the rest of the electrodes was illuminated. Again the effect was present, as was to be expected.

The conclusion arrived at from the various tests was that, in the first place, no effect is produced by light upon the conductivity of a fluorescent solution unless a region very near the electrodes is illuminated; and that further, this effect at the electrodes is only produced in a very thin film of the liquid immediately in contact with the surface of the plates.

It may be well to state that, while no reference has thus far been made to a variation of the effects in different parts of the spectrum, frequent tests were made in all of the experiments described, to see if the effects could be produced by parts of the spectrum which did not produce fluorescence. In all of these tests the effects obtained were either very feeble or entirely lacking. Thus, in the red, where the energy of the arc is the greatest, but where no fluorescence was to be detected, no effects were observed which were as great as 0.2 per cent either way. The frequent references to fluorescence in connection with the effects observed seem therefore to be entirely justified.

The next step undertaken in the investigation was a study of the variation of the effects at anode and kathode with varying potential difference at the terminals of the cell.

For this purpose the original form of cell was adopted, with electrodes 0.15 mm. thick and 3 mm. wide, placed next to the front wall of the cell and 3 mm. apart. The greater distance between the electrodes was adopted, so that while one of the plates was being illuminated no stray light could reach the other electrode. The greater thickness of the electrodes which, in view of the results of previous work could not materially affect the sensibility of the cell, served to keep the resistance of the cell as low as possible.

The screen in the front of the light-tight box *D* was so arranged that the cell could be moved into a position to expose either electrode to the light without having to raise the slide in the front of the box to make the adjustment.

As a source of E. M. F. a set of four sal-ammoniac cells was first used, but as these were found to drop slightly in voltage during a run, a pair of storage cells was substituted for them. The cells were connected to the ends of a rheocord, consisting of 10 meters of manganin wire, and sliding contacts were arranged so that any desired potential difference could be obtained at the bridge terminals, up to the limit of the cells.

To the bridge terminals were also attached leads from a large Weston milli-voltmeter, a resistance being placed in series with the meter, and the whole calibrated to a total range of 15 volts. With this arrangement it was found easy to obtain the potential difference between the terminals of the bridge with an accuracy of 0.01 of a volt, and any given value of the potential difference could be maintained constant throughout the time needed for the readings.

For greater simplicity in computation, and to make it possible to maintain the potential difference between the terminals of the cell at a constant ratio to the voltmeter reading, the bridge arms were arranged as follows (see Fig. 151): R_3 62,500 ohms, R_4 10,000 ohms, and R_1 a 100,000-ohm box to be used as the variable resistance. Thus, unless in a case where the resistance of the cell was so great that the 10,000-ohm box had to be varied, the fall of potential across the cell terminals was nearly 86 per cent of the voltmeter reading.

The change of resistance due to the illumination was estimated in two different ways, depending on the magnitude of the effect. If the galvanometer reading remained on the scale when the cell was illuminated, a reading of the deflection was taken. The illumination was then stopped and a second reading was taken and the two were averaged. A plug was then inserted in the 10,000-ohm box, the change of galvanometer reading obtained, then the plug was removed, a second reading taken, and the two averaged. Assuming that the galvanometer deflection was proportional to the change of resistance in the 10,000-ohm box, the number of scale divisions corresponding to a change of one ohm or one part in ten thousand was easily obtained. As increase or decrease in the apparent resistance of the cell would produce the same change in the potential difference at the galvanometer terminals as the same percentage decrease or increase of the resistance in R_4, it was easy to get quite satisfactory estimates of the change produced by the illumination. If the effect of the light was great enough to throw the galvanometer off the scale, a balance was restored by changing the resistance in R_1. The light was then shut off and a second balance was obtained, and from the average of the two changes in R_1 the change of resistance of the cell was calculated.

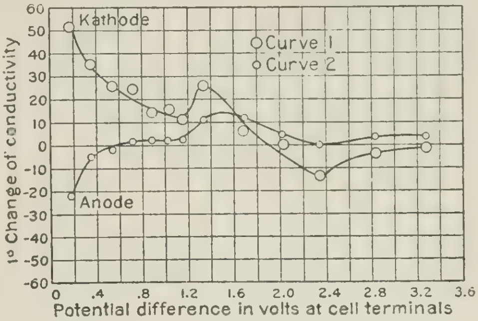

Fig. 156.

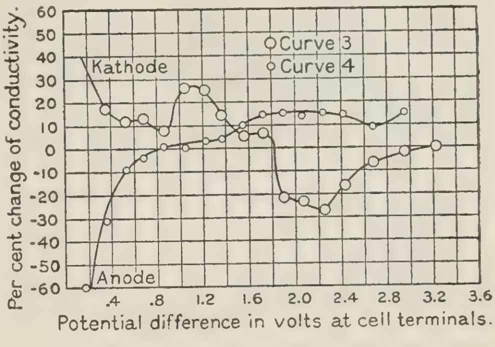

Fig. 157.

Curves were plotted, using potential differences at the cell terminals as abscissas, and change of conductivity, *i. e.*, reciprocals of resistance changes, as ordinates. Eight of these curves are shown in the accompanying figures. Each value of the conductivity change is the average of at least two readings, taken at intervals of 5 minutes time. These curves are typical of a large number that were obtained in a similar manner.

Owing to the variation in the intensity of the arc light used, and to the difficulty of setting up the cells in exactly the same manner each time, the magnitude of the effects obtained varies considerably in different curves. Nevertheless the character of the effects obtained did not vary greatly.

In curves 1 and 2, 3 and 4 (Figs. 156 and 157) the kathode and anode were illuminated alternately throughout the experiment. Each value of the change of conductivity is the average of at least two measurements, made at intervals of 5 minutes from the end of one measurement to the beginning of the next. It will be noticed that the kathode shows at low voltage a large decrease of resistance due to the light, followed by a considerable increase of resistance as the voltage rises. On the anode the effect at low voltage is just the opposite of that on the kathode and changes sign as the voltage rises as in the case of the kathode. It will be noticed also that the change of sign of the effect occurs considerably earlier in the case of the anode than in that of the kathode. The result is that for a considerable range of voltage both electrodes show a decrease of resistance with the light. As this region happens to include the voltage obtained when two gravity cells were used as the source of current, it is not surprising that a large decrease of resistance was observed in the first experiments, when both electrodes were exposed to the light at once.

As the curves showed that the effects on the two electrodes were in general of opposite sign, it was thought advisable to arrange a cell so that one electrode could be studied at considerable length, and with a certainty that no complications would be introduced by stray light reaching the other electrode.

In order to have the electrodes as far apart as possible, and still to keep the resistance of the cell within reasonable limits, the electrode to be exposed was alone fixed in the front of the cell, clamped to the front wall in front of and very near the edge of a narrow strip of glass. The other electrode was made L-shaped, nearly a centimeter being the length of each leg of the L cross-section. This electrode was placed in the main part of the cell with the base of the L toward the side of the cell away from the light source. This arrangement insured a very large electrode surface and also an average cross-section of the liquid between the electrodes sufficient to make up for the greater distance between them. It also served to concentrate the greater part of the resistance at the electrode to be illuminated.

As the kathode effect seemed the most promising for further study the current was sent through the cell from the large electrode to the one to be exposed.

A number of runs were made with this cell and from the results curves were plotted, of which 5, 6, 7, and 8 are typical specimens (Figs. 158, 159, and 160). It will be seen that the effects are considerably greater than those obtained in the former experiments, and also that the form of curve obtained is in general more regular than the others. The peculiar rise of the effect after the large decrease shown in the first part of the curve does not appear to be accidental, but is common to almost all the curves plotted for the kathode effect.

Curves 7 and 8 were made to ascertain the effect which the previous history of the cell might have on the action of the light. Curve 7 was obtained in the usual way, and a run was made immediately after without changing the cell, but beginning with high voltage and reducing the voltage by the same steps that had been used in going up.

It will be noticed that the curves are very much alike, the one taken on decreasing voltage showing a slight shift toward the right. For the last two points on the return curve it was found impossible to obtain a balance of the bridge, the condition of the cell appearing very unstable. At the three voltages 1.03, 1.21, and 1.38 of the first of these two curves a phenomenon was observed which occurred frequently throughout the experiments, at the point where the effect reversed. When the cell was first exposed the galvanometer showed an immediate decrease of resistance, followed in a few seconds, with the light still on, by a large increase. When the light was shut off the cell showed the two changes in the reverse order.

This would seem to indicate, at least in this region, a combination of two effects, one growing to a maximum more rapidly than the other, and dying away more slowly.

A few experiments were made with fluorescein in absolute alcohol, a trace of caustic soda being added to produce fluorescence. The effects obtained were very similar to those with the eosin, but not nearly as marked.

Rhodamin was also tried, with somewhat doubtful results, except that the effects with very low voltages were fully equal to those with eosin.

Since there seemed to be no doubt that the seat of the effect was the thin film of liquid in front of the electrode, and since the current could not be supposed to flow only to and from this film without entering the edge of the electrode, it did not seem possible to account for the changes in resistance observed, except by the actual creation of an electromotive force at the surface of the electrode or near it, by the action of the light. So long as low voltages were used, such an effect if it did exist would account for the change of resistance when either anode or kathode was illuminated. For suppose the E.M.F. produced to be such as to tend to make the exposed plate positive to the unexposed one. Then if the exposed plate were made the kathode with

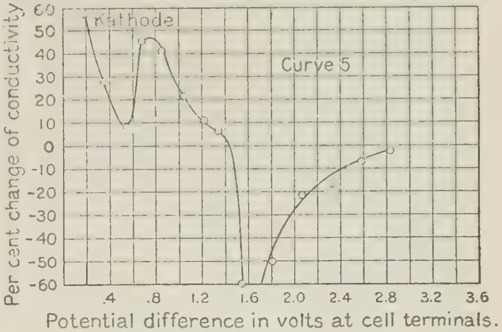

Fig. 158.

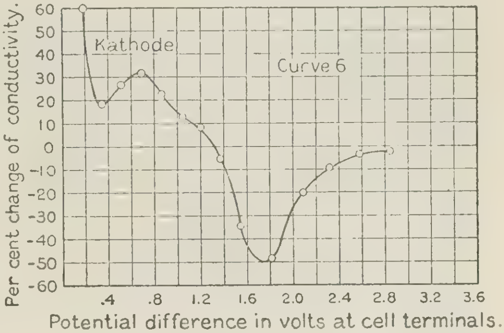

Fig. 159.

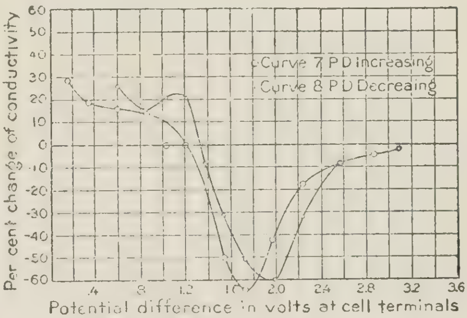

Fig. 160.

regard to the outside E.M.F., the E.M.F. due to illumination would act with the original E.M.F., producing a greater current through the cell and making its apparent resistance, as measured on the bridge, less.

If, on the contrary, the direction of the impressed E.M.F. were reversed, the photo-E.M.F. would oppose the passage of the current and the apparent resistance of the cell be increased.

The reversal of the effects when the voltage was raised is not easy to account for. From a number of tests of the polarization E.M.F. of eosin cells, made by comparing the E.M.F. with that of a standard cell by means of a condenser, the effect of maximum polarization appears to be a back E.M.F. of over 2 volts. This value determines the point where any considerable current begins to traverse the cell, and hence it would be most natural to expect that just here would occur any marked change in the phenomena, such as the reversal of the illumination effect. This, however, does not seem to be the case, for it will be noticed from the curves that the reversal in the case of the kathode occurs at very nearly 1.7 volts, while at the anode the voltage is much lower. That the effects at high voltages are connected in some way with the polarization of the cell seems, nevertheless, most probable, though in what manner has not as yet been determined.

Assuming that the effect at low voltage is due, as has been suggested, to a photo-E.M.F. similar to those which have frequently been observed in cells containing silver salts and many other electrolytes, attention was next turned to the effect of light on the cell when no external E.M.F. was applied.

The same type of cell was used as had been employed in all of the experiments on the kathode alone. The terminals of the cell were connected directly to the Sullivan galvanometer which had been used with the bridge in all the previous experiments.

Very considerable effects were produced by the action of the light, ample in magnitude to account for the phenomena observed with the bridge at low voltages.

A series of experiments was then undertaken to find if in any way this photo-electric effect was intimately connected with fluorescence.

In the first place tests were made throughout the visible spectrum, and curves plotted showing the variation of the current produced in the galvanometer as a function of the wave-length of the exciting light. The effect was found to increase regularly from the edge of the visible spectrum in the violet to a pronounced maximum just before the absorption band was left in going toward the red, namely, just at the infra edge of the green. The decrease of effect from this point on toward the red was very sudden indeed, and the effect was entirely lost before the edge of the visible spectrum was reached. Three other substances, namely, rhodamin, fluorescein, and naphthalin-roth were found to give similar effects, and in each one the maximum results were obtained at the infra edge of the absorption band. In rhodamin the effects were found to be enormously greater than with the eosin, but with the other two substances the results were less satisfactory.

With rhodamin tests were made by a condenser method to test the magnitude of the E.M.F. produced, and it was found to be as high as 0.2 of a volt. In eosin it is probable that the maximum was not over half that amount.

Dilute solutions of rhodamin were also tried with very good effects. The maximum dilution thus far tested is that of one part saturated solution to ten of alcohol.

With dilute solutions of eosin, however, the effects were greatly reduced. The extremely thin capillary film was found to be unnecessary, either in eosin or rhodamin, though the effects produced when the electrodes were more than 0.02 mm. back from the front of the cell were very small.

Tests were made of the absorbing power of both of the substances in saturated solution, and it was found that practically no light penetrated to a depth of 0.02 mm. in the region of the absorption band. Thus, if the effect is produced at the surface of the platinum plate itself, a film of this thickness or greater would completely screen the electrode from the action of the light.

The results obtained by Goldman, whose paper is referred to on page 151, agree in general with those of Dr. Hodge.

MR. HOWE'S[1] EXPERIMENTS ON FLUORESCENT ANTHRACENE VAPOR.

The following is an account of an attempt to determine whether fluorescence has any effect on the electrical conductivity of anthracene vapor. The expectation of a change in conductivity during fluorescence is based on the theory that fluorescence is a dissociation phenomenon. Although the results of the experiment were negative, it being impossible to detect any conductivity of the vapor either unilluminated or fluorescent, the accuracy of the work was such as to set a rather definite upper limit for any effect that may be present.

Little work has been done on the conductivity of vapors as affected by light. Henry[2] could find no conduction of iodine vapor due to light. On the other hand, J. J. Thomson[3] states, without giving reference, that light increases the conductivity of sodium vapor. Wiedemann and Schmidt,[4] in their paper in which they propose the dissociation theory, say that this does not call for any ionization in the case of fluorescent vapors.

The desirability of anthracene vapor for this experiment is seen from the following considerations:

1. The vapor is strongly fluorescent.
2. It has banded absorption and fluorescence spectra[5] lying in the region 320–400 $\mu\mu$, light of these wave-lengths being transmitted by the glass used in this experiment. Stark,[6] in his work on band spectra, has concluded that fluorescence and photo-electric properties are intimately associated with absorption in bands shaded toward the red, and that the "carriers" of the band spectra are the negative electrons, which are pulled out of their normal position by the incident light, and upon their return to the position of equilibrium liberate the energy of the fluorescent light.
3. If the separation of the electron is complete, photo-electric properties would be exhibited. It is thus that Stark and Steubing explain the fluores-

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[1] See H. E. Howe, Physical Review, xxx, p. 453.

[2] Henry, Proc. Camb. Soc., 9, p. 319, 1897.

[3] Thomson, Cond. through Gases, p. 213.

[4] Wiedemann and Schmidt, Ann. der Phys., 56, p. 201, 1895.

[5] Elston, Astr. Jour., 25, p. 155, 1907.

[6] Stark, Phys. Zeit., 8, p. 81, 1907.

cence of solid anthracene.[1] After investigating a number of substances, they say: "It is highly probable that for organic substances, at least, the photo-electric effect and fluorescence are intimately connected with each other." Hence it would seem that the vapor of anthracene would be as likely as any vapor to possess photo-electric properties.

APPARATUS.

The glass tube used to contain the anthracene is shown in Fig. 161. The larger part of the tube was 15 cm. long and 2.5 cm. in diameter. The electrodes between which the current passes consisted of an outer aluminum cylinder, to which connection was made by sealing a platinum wire through the glass at *M*, and an inner brass wire supported by a quartz tube *Q* and visible through the slit in the outer electrode.

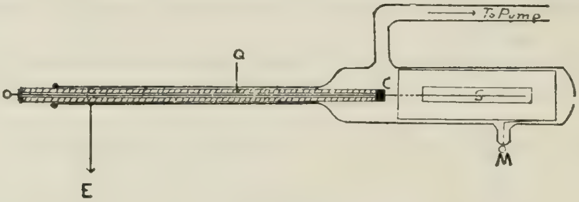

Fig. 161.

The quartz tube served as insulation for the brass wire electrode. Further protection was afforded by a deposit of silver on the inside of the glass tube around the quartz, this silver layer extending around to the outside of the open end, where it was wrapped with tinfoil and grounded to form a guard-ring. Thus no charge could leak over the glass surface from the outer electrode.

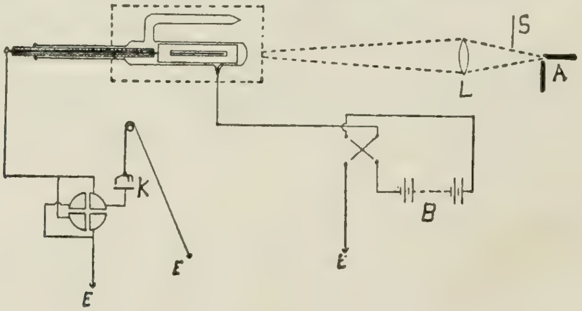

Fig. 162.

The openings at the outer end of the quartz tube were sealed with de Khotinsky cement. This would not stand heating, and the furnace was arranged to inclose only the large part of the tube (see dotted outline in Fig. 162). It was necessary to have the quartz tube fit snugly in place and to provide a tight-fitting cap *C* (Fig. 161) at the inner end in order to prevent the sublimation of the anthracene to the colder parts of the tube.

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[1] Stark and Steubing, Phys. Zeit., 9, p. 481, 1908. Also, Pochettino, Nuovo Cim., 15, p. 171, 1906.

The tube, after being charged with anthracene, was exhausted to a pressure of a few tenths of a millimeter, sealed off, and heated electrically. Light from a carbon arc *A* (Fig. 162) was converged by the lens *L*, and could be passed into the furnace through a mica window or could be cut off by the screen *S*. When the light was on, a bright cone of violet fluorescence could be seen in the center of the tube.

The outer electrode was charged from a storage battery *B*, and the rate at which the inner electrode acquired a charge was measured by means of a sensitive Dolezalek electrometer, which was inclosed in a wire cage to protect it from the electrostatic disturbances. The end of the anthracene tube projected through a hole in this cage, making the protection of the inner electrode practically perfect.

OBSERVATIONS AND RESULTS.

The electrometer needle was charged to a constant potential (in most of the work this was 60 volts), one pair of quadrants was grounded, and the other pair connected to the wire electrode. This pair could be grounded or insulated at will by means of the key *K*. When *K* was raised the motion of the needle was noted by observing on a ground-glass scale the image of a lamp filament formed by the small concave electrometer mirror.

If V_q be the potential of the charging quadrants; K the deflection when V_q is 1 volt; C the capacity of the charging system; Q the charge; D the deflection; and I, the current; then

$$D = k \times V_q \quad \text{and} \quad Q = CV_q$$
$$I = dQ/dt = C \times dV/dt = k \times C \times dD/dt$$

on the assumptions that k[1] is the same for the moving needle as for the needle at rest and that C does not change with the position of the needle. Such assumptions are allowable for slow motion and small deflections.

C was determined by dividing the charge with a cylindrical condenser of 30 cm. capacity, and was found to be 45 cm. or 5×10^{-5} microfarads.

A charging rate of 1 division per second could easily be observed if definite. This would mean a current 1.3×10^{-13} amperes. The insulation was such that the rate of leak when charged to 50 divisions deflection was about 10 divisions per minute, or one-sixth the rate mentioned as easily measurable for charging.

At the low pressure used, anthracene vaporizes sufficiently to show fluorescence between 200° and 250° C. "90 per cent sublimed" anthracene was used without attempt at purification, as it was easily obtainable and the presence of impurities in the material does not seem to affect the fluorescence of the vapor. No attempt was made to shield the electrodes from the light scattered by the end of the tube, nor to use monochromatic light.

In liquids there is a photo-electric effect, as has already been shown in this chapter, dependent upon which of the electrodes is illuminated. The possibility of the existence of such an effect in the vapor was not here considered.

In most of the work the outer electrode was charged to 120 volts from an ordinary storage battery. *K* was raised and the rate of motion noted for the unilluminated tube. This was repeated with the light on.

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[1] When the potential of the needle was 60 volts the value of *k* was found to be 375 mm. on a scale one meter distant.

When the tube was newly made up the electrometer remained quiet under all conditions, except for an occasional drift of not more than 1 division in 5 seconds. In the earlier work, after a few heatings, the electrometer began showing a tendency to rise rather quickly to a more or less definite deflection, regardless of conditions of potential or illumination. This peculiar effect varied from run to run and became very great in a case or two when the cement with which the tube was sealed cracked and admitted air. A brown deposit was then left in the tube, apparently the result of a combination of the oxygen of the air with the anthracene.

A possible explanation of this attainment of a steady deflection even when the outer electrode was earthed is that the product of the decomposition of the anthracene is deposited on the quartz tube separating the silver guard-ring from the inner electrode and forms with these two metals a sort of voltaic cell. This "cell" had a very high temperature coefficient and in some cases the E.M.F. was so great as to throw the spot of light off the scale.

After several trials it was found possible, by taking great care to prevent the entrance of air, to get almost entirely rid of this effect. The electrometer then behaved normally.

No ordinary conduction was found. If the light had any effect it was too small to be detected. Thinking that the vapor under the action of the light might be almost ionized, an attempt was made to help out the ionization by exposing the vapor to the action of a small sample of radium bromide. The ionizing rays from this substance did not pass through the glass sufficiently to be of any use.

Higher potential was obtained by making up a set of small lead sulphuric acid storage cells in test-tubes. This battery, when put in series with the one already at hand, gave from 360 to 540 volts, depending upon the condition of the small cells. The sensibility was increased by charging the electrometer needle to 120 volts. With the greater sensitiveness and the unsteady potential furnished by the cells, the electrometer wandered more or less in the neighborhood of the zero, but still did not indicate any steady rate of charging such as would have been evident had there been appreciable conductivity of the vapor.

In the freshly exhausted tube the pressure was so low that the application of 400 volts caused a continuous luminous discharge through the tube, but this soon disappeared as the pressure rose due to the vaporization of the anthracene.

The number of trials was great enough to leave no doubt as to the behavior of the vapor under the various conditions mentioned.

CONCLUSIONS.

1. The conductivity of anthracene vapor at the temperature and density used in this experiment is too small to measure in the manner described.

2. The effect of fluorescence, if any exists, is too small to be detected by the very delicate method employed.

CHAPTER XI.

ON FLUORESCENCE ABSORPTION.[1]

In a paper published in 1904[2] we used the term fluorescence absorption in referring to the increase of the absorbing power of a fluorescent substance which results from fluorescence. Such an effect was first observed by Burke,[3] who found a considerable increase in the absorption of uranium glass when the glass was excited to fluorescence. The present writers observed the same effect in solutions of fluorescein and eosin. The increase in the absorption appeared to be greater for those wave-lengths which corresponded to the brightest regions of the fluorescence spectrum. Camichel,[4] upon repeating these experiments, was unable to detect any change of absorbing power during fluorescence either in the uranium glass used by Burke or in the fluorescent solutions tested by us. The question was again attacked in 1907 by Miss Wick,[5] who made a detailed study of the phenomenon in the case of an alcoholic solution of resorufin. Her results consistently showed an increase in the absorbing power of the solution during fluorescence, and were in complete agreement with the results obtained by us with fluorescein and eosin. More recently a method of detecting the effect, if it exist, has been suggested by Wood,[6] and a few trials of the method by him led to negative results. The most recent experimenter in this field is Houstoun,[7] whose very careful experiments also fail to give any indication of a change in absorption due to fluorescence.[8]

The results obtained by ourselves, and especially those obtained by Miss Wick, were so definite and positive that until recently we have been of the opinion that the failure of others to observe the effect was due to the fact that they had not chosen suitable conditions for the experiment. We were led to suspect the existence of some systematic error, however, by the results of a careful study of the collimator slit of the spectrophotometer used in our experiments upon the distribution of energy in fluorescence spectra.[9] It was found that the screw was a very accurate one and that the opening of the slit was very closely proportional to the reading of the micrometer screw. To test this point the slit was mounted in a lantern and the enlarged image was measured for a large number of different settings. The results are shown in Fig. 163.

We then tested the amount of light passing through the slit at different widths by balancing two acetylene flames against each other, the adjustment being made by varying the slit width in one case and by varying the dis-

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[1] Nichols and Merritt, Physical Review, XXXI, p. 500, 1910.
[2] Nichols and Merritt, Physical Review, XIX, p. 397, 1904.
[3] Burke, Philosophical Transactions, 191a, p. 87, 1898.
[4] Camichel, Comptes Rendus, vol. 140, p. 139.
[5] Frances G. Wick, Physical Review, XXIV, p. 407, 1907.
[6] R. W. Wood, Phil. Mag., 16, p. 940, 1908.
[7] R. A. Houstoun, Proc. Royal Society of Edinburgh, 29, p. 401, 1909.
[8] Since the work described in this chapter was first published, still another article on the subject has appeared, in which the results were also negative.
[9] See Chapter XII.

tance of the flame in the other. The experiments were performed in a dark room with an elaborate system of screens to prevent reflections, and several independent tests convinced us that the inverse-square law of distances was very exactly satisfied. If the intensity is computed by the law of inverse squares, and if a curve is plotted showing the relation between intensity and slit width, the results obtained are of the type illustrated in Fig. 164.

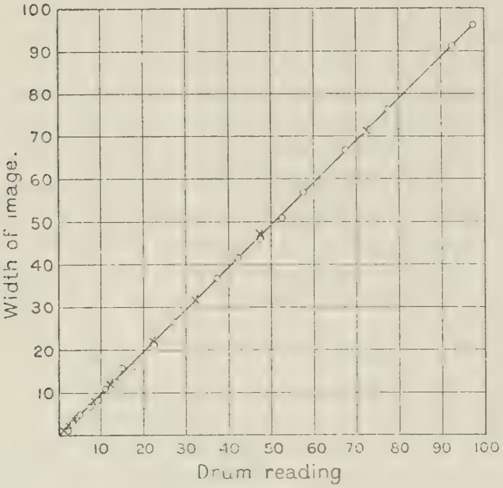

Fig. 163.

It will be seen that for narrow slits the intensity of the transmitted light is not proportional to the slit width. When the width exceeds a few hundredths of a millimeter the line becomes straight, so that equal increments in slit width correspond to equal increments in intensity. The conditions, whatever they are, which lead to the curve in the neighborhood of the zero of Fig. 164 are equivalent in their effect to a shift in the zero point of the screw by about 2 divisions. The intensity transmitted by a slit 50 divisions wide is not twice as great as that transmitted by one 25 divisions wide, but the ratio is in reality 48 to 23.

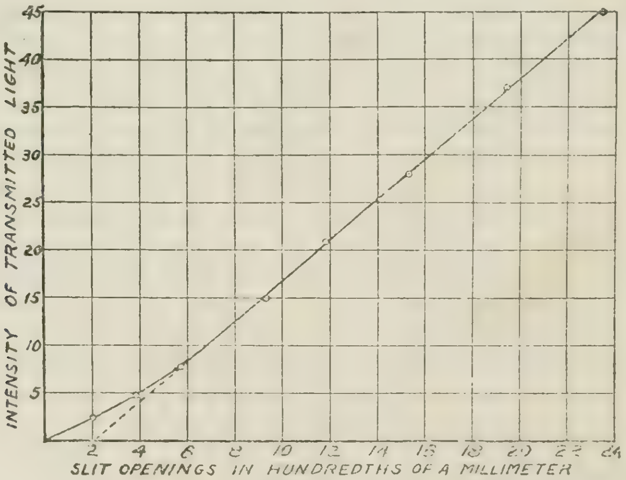

Fig. 164.

These experiments were not made with the same instrument that had been used by ourselves and later by Miss Wick, but refer to an exactly similar Lummer-Brodhun spectrophotometer. It seems probable that this effect, due possibly to diffraction or to reflection from the jaws of the slit, is common to all instruments of this type. It is clear that if the effect is disregarded, indications of fluorescence absorption may be obtained even if no such effect exists. The method used by Miss Wick and by ourselves involved three readings, namely, the intensity of the fluorescent light alone, the intensity of the light transmitted by the solution when not excited, and the combined intensity when light was transmitted through the solution at the same time that the latter was excited to fluorescence. The sum of the first two readings being found greater than the third, it was assumed that the transmission in the latter case was less than in the first. If, however, each of these readings of intensity had been too great by 2 divisions, as indicated by Fig. 164, the result of such procedure would be to give an apparent fluorescence absorption measured by 2 divisions.

While it is difficult to see how this source of error alone could account for results of the character obtained by Miss Wick and ourselves, the detection of one source of systematic error made it appear possible that other similar errors might be present, and led us to take up the study of this question anew. The result of the numerous experiments which will be briefly described in this chapter has been to convince us that the phenomenon of fluorescence absorption either does not exist, or that the effect is so small that the methods thus far used for its detection are inadequate.

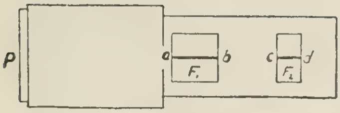

Fig. 165.

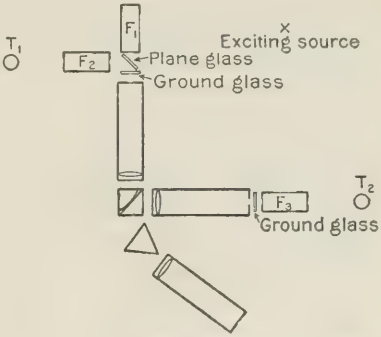

Fig. 166.

In the first method used an attempt was made to obtain a photographic record of the effect. The arrangement is shown in diagram in Fig. 165. The large square cell F_1, containing a solution of fluorescein, was excited from above by a narrow beam of light, so that a central layer *ab* was excited while the rest of the solution was not. Directly back of this was another cell F_2, also illuminated from above, so that the narrow vertical strip *cd* was excited. The photographic plate *P*, suitably screened from all sources of light except the fluorescence in F_1 and F_2, would be fogged nearly uniformly over its surface by the light from *ab* if this alone was excited, and the fogging would also be practically uniform if *cd* was excited. If, however, that part of the liquid in F_1 which is excited to fluorescence acquires the power of absorbing the fluorescent light more strongly than before, then we should expect *ab* to cast a shadow upon the photographic plate. While this shadow could not be expected to be very sharp or very dense, the results obtained by ourselves and Miss Wick indicated that under suitable conditions it ought to be clearly visible in the negative.

Extended efforts were made to obtain such conditions of concentration, thickness of layer, intensity of excitation, etc., as would bring out the expected shadow on the plate P. Over 100 negatives were made and many of these were under conditions which appeared to us to correspond to those under which the spectrophotometer had indicated a large fluorescence absorption; but in no case was a definite shadow observable.

The next method of testing the matter is shown in diagram in Fig. 166. Three cells containing a solution of fluorescein, or in some cases resorufin, were used as shown in Fig. 166. F_1 and F_3 were excited by the same source so as to eliminate errors due to variations in excitation; the source used was sometimes a quartz mercury lamp and in other cases the tungsten lamp. Since the solution was exactly the same in all three cells, and since F_1 and F_3 were at nearly the same distance from the exciting source, the two collimator slits were illuminated with almost equal brightness. Any slight inequality was balanced by opening or closing one of the slits. This adjustment being made, the exciting source was extinguished and light was sent through the cell F_3 from a small tungsten lamp T_2. To balance this illumination, light from another tungsten lamp, after passing through the cell F_2, was reflected by a piece of plane glass into the second collimator slit. The balance was obtained by adjusting the distance of T_2, which slid upon a graduated photometer track. When this balance was obtained the exciting source was again started and the field of the spectrophotometer observed. If the effect of fluorescence is to increase the absorbing power of F_3 we should expect that while fluorescence alone and transmission alone give a perfect balance, there would be a lack of balance when excitation and transmission occur simultaneously. When satisfactory conditions of steadiness were obtained no such disturbance of balance could be observed. A sample set of readings is given in Table 20. The small positive result obtained in this case is smaller than the errors of observation. In other cases the results indicated a small decrease in absorbing power during fluorescence. The experiment was tried with solutions of different concentration and different intensities of excitation. But when satisfactory conditions as regards steadiness were obtained no disturbance of balance could be detected which was greater than the errors of observation.

TABLE 20.

Resorufin. Excited by Mercury Arc.

Slit in front of F_3 set for equality of fluorescence alone. Readings 51.6, 49.7, 50.7, 50.7. Slit set at the average 50.7.
Lamp T_2 set for $F+T$, *i. e.*, fluorescence and transmission together. Distances =233, 245. Average 239.
Lamp T_2 set for transmission alone (T) 233, 233. Average 233.
$F+T$, 226, 228. Average 227.
Slit set again for equality of fluorescence alone. Readings 50.7, 50.4, 50.3, 50.7. Slit set at the average 50.3.
$F+T$: 235, 239. Average 237.
T: 243, 245. Average 244.
$F+T$: 226, 237. Average 232.
Slit set for F alone: 50.8, 50.8, 50.7, 50.6. Average 50.8.
$F+T$: 238, 243. Average 240.5.
T: 240, 236. Average 238.
$F+T$: 243, 237. Average 240.
Average of all: Distance of lamp for T alone =238.3; for $T+F$=236.0.
If this difference is real it indicates that the absorption of the solution during fluorescence exceeds its absorption when unexcited by 1.7 per cent.

It was suspected that the phenomenon of fluorescence absorption apparently demonstrated by Miss Wick and ourselves might indicate not an increase in the absorbing power of the solution but rather a decrease in its power of fluorescing. The results obtained by us might be interpreted equally well in either of these two ways. The fact that fluorescence absorption seemed to be in proportion to intensity of fluorescence in different parts of the spectrum lent strength to this view. If the effect is a diminution of fluorescence and not an increase in absorption the failure of our photographic tests could also be explained in an obvious manner.

If the fluorescence is diminished we should expect the diminution to be observable not only along the line of the transmitted light but in other directions. To test this matter we set up two large fluorescent cells F_1 and F_2 (Fig. 167) covered with black paper except on the sides toward the exciting mercury arc, and having two openings O_1 and O_2 in the bottom through which the light of the tungsten lamps T_1 and T_2, after reflection from mirrors, might pass up into the cell. The balance having been obtained with fluorescence alone, the lamp T_1 was then turned on and we tried to determine whether there was any change in the balance resulting from extinguishing T_1 and at the same time lighting T_2. The only effect was a slight one, opposite in sign to that which would be indicated in fluorescence absorption, and due undoubtedly to a small amount of stray light entering the slit after reflection from the walls of the cell.

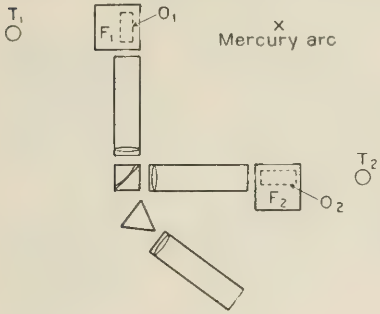

Fig. 167.

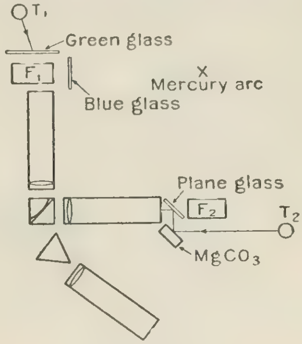

Fig. 168.

It seemed to us possible that the effect might be analogous to the effect of infra-red rays in suppressing fluorescence, and that possibly it might be produced not by the visible rays which caused this annoyance through stray reflection, but by the red or infra-red rays. We therefore interposed ruby glass in the path of T_1 and T_2, thus eliminating disturbances due to stray light. Under these circumstances no disturbance of balance resulted from extinguishing one lamp and lighting the other.

It seemed possible that while fluorescence absorption might really be the result of a diminution in the intensity of fluorescence this decrease might not be the same in all directions, but might be greatest in the direction in which transmitted light proceeded. The arrangement of apparatus shown in Fig. 168 was intended to test for the effect in directions nearly but not quite the same as the direction of transmitted light. The light from the tungsten lamp T_1 passes through the cell F_1 so as not to fall in the slit of the instrument, but being nearly parallel to the axis of the collimator. The small amount of stray light from T_1 which unavoidably did reach the slit was balanced by light from the second tungsten lamp T_2 as shown in the figure. The results were entirely negative. Thinking that the intense green line of the mercury arc might produce so much effect in weakening the fluorescence in F_1 that additional light from T_1 would produce only a slight effect, we interposed in some cases blue glass as shown, and in order to diminish the excitation produced by the light from T_1 we sometimes used green glass as indicated. The results, however, were in all cases negative.

In Fig. 169 is shown an arrangement for testing the effect of transmitted light upon fluorescence in case the direction of transmission is opposite to the direction in which fluorescence is observed. No effect could be detected.

In Fig. 170 are shown the essential parts of an apparatus used in applying the method suggested by Wood.[1] A disk, shown in detail at the right of the figure, was arranged so that the four sectors might either occupy the position shown in the upper diagram, or might be shifted with reference to each other so that the inner openings and the outer openings would be alternate. This disk was mounted between the exciting source and the fluorescent cell F, as shown. Light passed through the outer sectors to excite fluorescence, and light passing through the inner sector, after reflection from a block of magnesium carbonate, passed through the cell to the collimator slit. Having balanced the illumination against a standard placed before the second collimator for the case where the inner and outer sectors were open alternately, the disk was then changed so as to make the excitation and transmission simultaneous. The results of several sets of observations with this apparatus are given in Table 21. The observations indicate a slight *negative* effect, that is, the transmission of the solution appears to be greater during fluorescence. But the effect indicated is so small that we are inclined to look upon it as resulting from accidental errors.

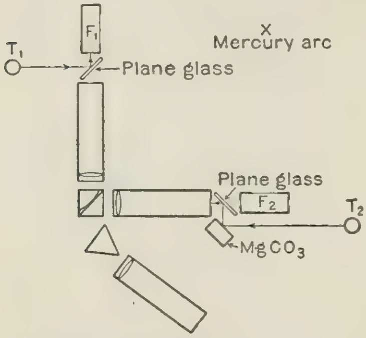

Fig. 169.

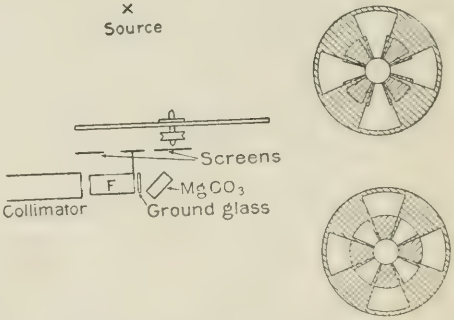

Fig. 170.

A few measurements were made by a method essentially the same as that used by us in 1904, except that the source of the light transmitted was the fluorescence of a portion of the solution. A dilute solution of fluorescence was contained in a cell 20 cm. long, so arranged that either the half nearest

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[1] R. W. Wood, Philosophical Magazine, p. 940, 1908.

the slit or that at a distance could be screened from the exciting light, which in this case was the mercury arc. The spectrophotometer was set for a wave-length near the crest of the fluorescence spectrum and not overlapping either of the mercury lines, so that errors due to stray light were excluded. Upon screening that part of the cell lying nearest the slit the field was illuminated by the fluorescence light of the distant part of the cell after transmission through the rest of the cell *T*. Upon screening the distant part of the cell the light received in the instrument was due to the fluorescence of the nearer part *F*. Upon removing both screens fluorescence and transmission occurred at the same time *C*. If absorption is increased by fluorescence we should have

TABLE 21.

The numbers in the table give the width of the slit near *F* (Fig. 170) when set to a balance with the standard in front of the other slit.

Fluorescein. Moderate concentration. Wood's method. $\lambda=0.523\mu$		*Resorufin. Dilute. Wood's method.* $T=1.02F$. $\lambda=0.599\mu$	
Sectors open alternately.	Sectors open at same time.	Sectors open alternately.	Sectors open at same time.
100.9	101.2	64.6	66.2
97.7	100.2	65.2	64.4
104.2 Av. 101.58	100.5	67.3	65.4
103.5	101.2 Av. 100.78	66.8 Av. 65.98	65.7 Av. 65.42
100.5	102.0	66.6	66.8
101.7	98.8	66.4	65.9
100.0	100.7	66.5	66.2
100.4 Av. 100.65	98.7 Av. 100.05	66.9 Av. 66.68	66.3 Av. 66.30
Final av. = 101.11	Final av. = 100.41	Final av. = 66.33	Final av. = 65.86
		Fluorescence absorption $=-0.014T$.	

Resorufin. Dilute. Wood's method. $T=0.18F$. $\lambda=0.599\mu$		*Resorufin. Dilute. Wood's method.* $T=7.27F$. $\lambda=0.599\mu$	
113.4	111.2	20.6	19.0
112.2	112.4	20.1	19.4
114.7	112.3	20.6	19.8
Av. 113.4	111.9 Av. 111.95	20.1 Av. 20.35	20.0 Av. 19.78
112.4	112.3	20.3	20.0
113.8	113.7	19.9	20.3
113.3	113.4	20.4	20.5
114.7 Av. 113.7	112.8 Av. 113.05	20.4 Av. 20.25	20.7 Av. 20.38
Final av. = 113.55	Final av. = 113.0	Final av. = 20.30	Final av. = 20.08
Fluorescence absorption $=-0.033T$.		Fluorescence absorption $=-0.012T$.	

$$F+T>C$$

The readings in one case are given in Table 22.

TABLE 22.

	F		T		C
	23.7		23.2		
	23.7		23.4		
	22.9		23.6		41.2
	23.4		22.9		41.2
Average	23.42	Average	23.28	Average	41.2
Zero	2.4		2.4		2.4
	$F=21.02$		$T=20.88$		38.8

$$F+T-C=41.9-38.8=3.1=0.15T.$$

The observations contained in Table 22 indicate a positive fluorescence absorption of 15 per cent. But if we apply the additional zero correction called for by the calibration curve of Fig. 164 the difference between $F+T$ and C is reduced to 0.9 division or 4.3 per cent. In other cases an equally large negative result was obtained.

The results of all of these experiments, which have been repeated many times, and performed with more precautions to avoid false results than can be indicated in this brief account, has been to convince us that the previous results of both ourselves and of Miss Wick are due to some systematic error, and that the supposed increase in absorption due to fluorescence either does not in reality exist or is too small to be detected by these methods. We have not been able to determine the exact nature of the error which led to our preceding results. The peculiar relation between slit opening and intensity brought out in Fig. 164 will explain some of the results but not all. Another source of error which might have been an important one is that resulting from the neglect of the slit-width correction, to the importance of which attention is directed in Chapter XII of this memoir.

CHAPTER XII.

THE DISTRIBUTION OF ENERGY IN FLUORESCENCE SPECTRA.[1]

The energy of most continuous spectra is too feeble to permit of accurate measurements excepting in the infra-red and the longer wave-lengths of the visible spectrum, although we have a few determinations of the energy of the visible spectrum of the acetylene flame by G.W. Stewart[2] and by Coblentz[3] that extend beyond the green. The direct measurement of the energy of even the brightest of fluorescence spectra, which are very small in intensity as compared with those of our ordinary artificial light sources, is therefore impracticable. We have shown, however, in previous chapters of this memoir that it is possible to make quantitative spectrophotometric comparisons between fluorescence spectra and the spectrum of a standard such as the acetylene flame. If the distribution of energy of the source used for comparison be known, it is therefore easy to compute that of the fluorescence spectrum. We have adopted this method in determining the energy distribution in the fluorescence spectra of fluorescein, eosin, and resorufin, with the results recorded below. The experimental work naturally falls under three heads: (1) The determination of the energy distribution in the standard source; (2) the spectrophotometric comparison of the fluorescence spectrum with the standard; (3) the measurement of the absorption of the fluorescent liquid, in order that the observed curve of fluorescence may be used to compute the typical curve.

DETERMINATION OF THE DISTRIBUTION OF ENERGY IN THE SPECTRUM OF THE COMPARISON FLAME.

The comparison source used in the experiments to be described in this paper was an ordinary flat flame from an acetylene burner, in front of which, at a distance of 1.4 cm., was mounted a metal screen having a circular hole 0.6 cm. in diameter, so as to cut off the light from all but the brighter central portions of the flame. This flame with its diaphragm was mounted in a metal box having a circular window opposite the diaphragm. The box was fastened to a base fitted to slide along a straight metal track. This track was mounted horizontally in the same vertical plane as the axis of one of the collimators of a Lummer-Brodhun spectrophotometer, and at such a height that the axis of the collimator extended would pass through the window in the box and through the center of the diaphragm to the flame itself.

In front of the slit of the collimator was mounted a sheet of clear white glass, the surface of which had been sufficiently roughened by grinding with powered carborundum, so that at whatever distance the flame might be placed the contrast field of the spectrophotometer would be of uniform brightness throughout. The loss of light by the interposition of the ground

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[1] The contents of this chapter first appeared in the Physical Review, XXX, p. 328.

[2] G. W. Stewart, Physical Review, XVI, p. 123.

[3] W. W. Coblentz, Bulletin of the Bureau of Standards, VII, p. 243.

glass was found to be about 40 per cent. Its transmission throughout the range of wave-lengths used in our measurements was not measurably selective.

To determine the distribution of energy in the spectrum of the light received from the comparison flame after passing through the ground glass and the optical parts of the spectrophotometer, this spectrum was carefully compared wave-length by wave-length with the light received through the other collimator of the instrument from a black body of known temperature.

The black body, Fig. 171, consisted of a tube of Acheson graphite about 50 cm. long, of 1.7 cm. bore and 4.0 cm. external diameter. In the middle this tube was turned down for about 20 cm. until the thickness of the walls was reduced to about 0.4 cm. and the thin-walled cylindrical chamber thus formed was heated by means of an alternating electric current furnished by a step-down transformer, of whose secondary circuit it formed the principal part.

The ends of the cylindrical body were graphite plugs, each with an axial hole 1 cm. in diameter. Through one of these passed a tube of fused quartz containing a platinum-rhodium-platinum thermo-junction of wires which had been calibrated at the Bureau of Standards. This junction received radiation from the surrounding walls and could be pushed in and out at will so as to ascertain the range of temperatures within the black body. Through the opening in the other plug and through corresponding openings in diaphragms located nearer the ends of the graphite tube, light from the incandescent tip of the quartz tube reached the spectrophotometer.

Fig. 171.

To reduce heat losses and prevent the too rapid oxidation of the graphite, the tube was embedded to a depth of about 8 cm. in a mass of powered magnesite, which was contained in a hollow cylinder of magnesium oxide and asbestos such as is used for the packing of large steam pipes.

When the primary circuit was supplied with 80 amperes at 110 volts the temperature of this improvised furnace, as indicated by the thermo-junction, rose slowly to nearly 1500° C., at which temperature it remained with little change for a considerable time. Temperatures were determined in the usual way by means of a potentiometer and cadmium cell.

The arrangement of the apparatus is shown in Fig. 172, in which *R* is an adjustable resistance, *A* is an a. c. ammeter, *P* is the primary coil of transformer, *S* is the secondary coil, *D* is a Dewar flask with the cold junction in ice, *a* and *b* are the collimator slits of the spectrophotometer, *L* is the Lummer-Brodhun prism of the spectrophotometer, *O* is the observing telescope of the spectrophotometer, *g* is the ground glass in front of slit *b*.

The slits *a* and *b* were set once for all to convenient widths, *b* being 30 divisions =0.6 mm. in width, and *a* 0.06 mm. The adjustable diaphragm in *O* was of the same width as slit *b*.

In this determination one observer made settings for wave-length and watched the contrast fields of the spectrophotometer, while another recorded the positions of the comparison flame when, for each region of the spectrum, equality had been reached. In the meantime a third observer followed the changes of temperature with the potentiometer and recorded the E.M.F. of the thermo-junction for each setting of the spectrophotometer. Readings were begun when a temperature of 1410° (absolute) was reached. Subsequently the current was slightly reduced and further sets of readings were made throughout the spectrum.

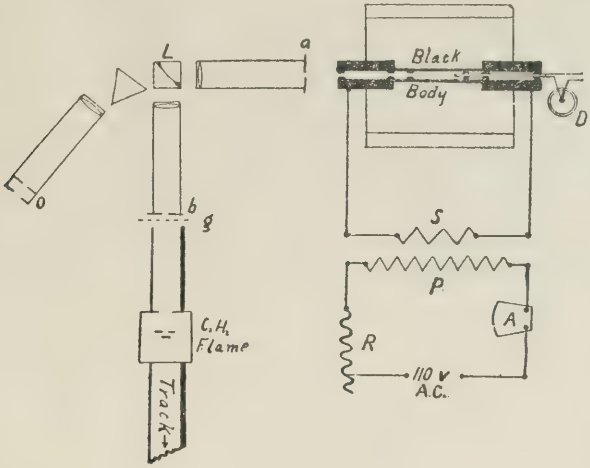

Fig. 172.

From these data the distribution of energy in the spectrum of the comparison flame was computed.

Wien's equation

$$I_\lambda = C_1 \lambda^{-5} e^{-\frac{C_2}{\lambda T}}$$

was taken as giving the energy in the region of the spectrum at which measurements were made. The accepted value, for an ideal black body, of the constant C_2 (*i. e.*, $C_2 = 14{,}500$) was assumed to be applicable to the present case, and the quantity $C_2/\lambda T$ was calculated from the readings of wave-length and temperature. Since relative values only were desired, the constant C_1 was given a value convenient for purposes of computation.

TABLE 23.

Wave-length.	$I_\lambda/(1/d^2)$	Wave-length.	$I_\lambda/(1/d^2)$
0.656	248.0	0.534	58.70
.628	189.0	.521	48.50
.604	149.2	.508	42.50
.583	112.9	.497	37.73
.565	87.0	.486	29.33
.548	69.2	.477	21.25

The two slits of the spectrophotometer were maintained at a constant width throughout, and the distance (d) of the comparison flame was varied until the intensities of the spectra were equal. The energy of any given region of wave-length λ was therefore proportional to the ratio $I_\lambda/(1/d^2)$ where I_λ was the energy of the corresponding region of spectrum of the light from the black body, computed as above.

Observations were made for twelve regions lying between 0.477 μ and 0.656 μ, and in the course of the determination the spectrum was traversed four times. Good agreement existed between the various readings in each region with the exception of the observations immediately following changes made in the resistance of the primary circuit. These were rejected and all other readings were used in the computations and averaged for each wavelength separately. The results are given in Table 23 and are shown graphically in Fig. 173.

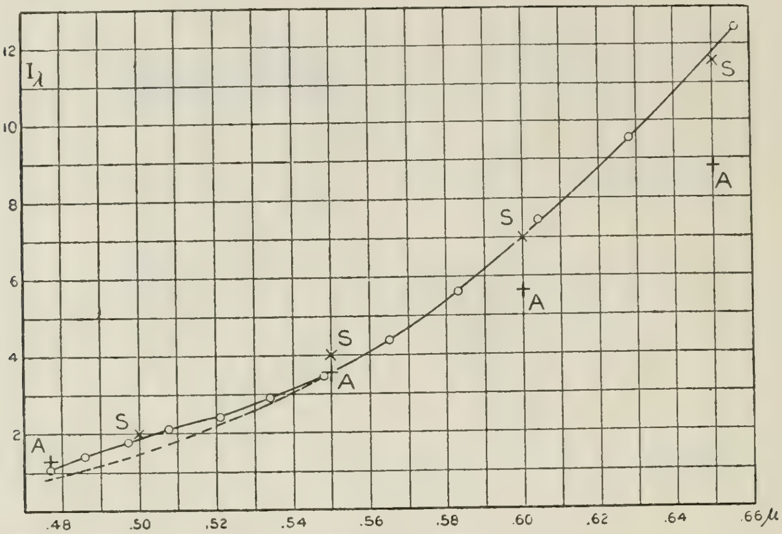

Fig. 173.

Distribution of energy in the spectrum of the acetylene flame. The points marked *S* correspond to Stewart's direct measurements with the radiometer. The points marked *A* are derived from Ångström's measurements of the Hefner lamp. The dotted line is computed from Wien's equation.

TABLE 24.

Spectrophotometric comparison of the acetylene comparison flame, viewed through the circular diaphragm and ground glass, with flame of a Hefner standard lamp.

λ	C_2H_2/Hefner.		C_2H_2/Hefner.
0.656μ	0.916	0.534μ	1.32
.628	.950	.521	1.43
.604	.990	.508	1.53
.590	1.00	.495	1.69
.583	1.04	.487	1.83
.565	1.11, 1.15	.477	1.90
.548	1.25		

Wien's equation has been employed, although in quite a different way, by Knut Ångström[1] for the determination of the distribution of energy in the spectrum of the flame of the Hefner lamp, and it is of considerable interest to compare his determination, which involved neither the direct measurement of temperatures nor observations upon a black body, with the results of the experiment just described.

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[1] Ångström, Nova Acta Upsaliensis, III, vol. XXII, 1904.

For this purpose we made a careful spectrophotometric comparison between our acetylene standard and a Hefner flame (see Table 24 and Fig. 174). From Ångström's curve of the distribution of energy in the spectrum of the Hefner standard we then computed the relative intensities of our comparison flame for several regions lying between 0.656 μ and 0.483 μ. The points so determined are shown in Fig. 173 by crosses marked *A*.

Several points determined by Stewart by direct measurement with the radiometer are also shown in Fig. 173, being marked *S*.

It is a matter of some interest to determine to what extent the visible radiation from the acetylene flame corresponds to the visible radiation from a black body. We find that the curve computed from Wien's equation is practically identical with our experimental curve from 0.56 μ to 0.65 μ. But for wave-lengths less than 0.56 μ the curve based upon Wien's equation (shown by the broken line in Fig. 173) deviates considerably from that determined by experiment. The acetylene flame appears to possess a band of abnormally high radiating power in the region lying between 0.55 μ and the violet end of the spectrum.

Since the first account of our own work appeared Coblentz[1] has published the results of direct measurements of the spectrum of the acetylene flame with the vacuum bolometer. While Coblentz's results are in fair agreement with ours in the region from 0.48 μ to 0.56 μ, they differ very appreciably for the longer waves, lying between our own results and those of Ångström.

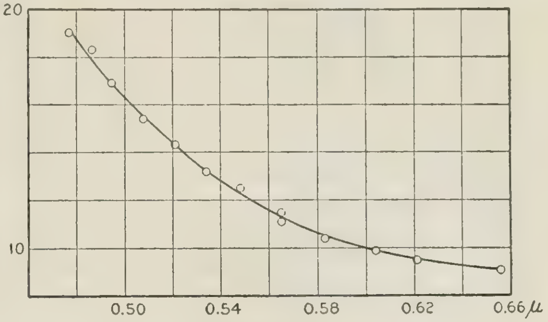

Fig. 174.

COMPARISON OF THE FLUORESCENCE SPECTRA WITH THE SPECTRUM OF THE STANDARD ACETYLENE FLAME.

Before making the final spectrophotometric determinations from which the distribution of energy in the spectrum of various fluorescence spectra were to be computed, a careful study was made of the effect of slit-width upon the form of the observed curves.

In the ordinary use of the Lummer-Brodhun spectrophotometer slit *a* (Fig. 172) would be of constant width and slit *b* would be varied. The accuracy of the screw of the latter was therefore tested, as already described at length in the opening paragraphs of Chapter XI, by mounting the slit, which had been removed from the instrument, in the field of a projecting lantern and measuring the width of the slit-image, focused upon a horizontal millimeter scale at a distance of about 8 meters. Variations from constancy of the ratio of widths to micrometer readings were found negligible for a range of two turns of the screw. Studies of the brightness of the spectrum obtained when this slit was used showed, however, marked

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[1] Bulletin of the Bureau of Standards, vol. 7, p. 243, 1911.

deviations from the expected proportionality between the slit-width and intensity, especially for widths of less than 0.01 cm. (see Figs. 163 and 164 in Chapter XI).

It was therefore decided to avoid changes in slit width by using the method of comparison used in determining the distribution of energy in the spectrum of the comparison flame. In this method the two slits of the spectrophotometer remain unchanged in width, and equality of brightness is obtained for each region of the spectrum by moving the comparison flame along a bar or track parallel to the axis of the collimator. With the system of screens which we employed to exclude stray light, the law of inverse squares was found to hold for the entire range of distances used in our experiments.

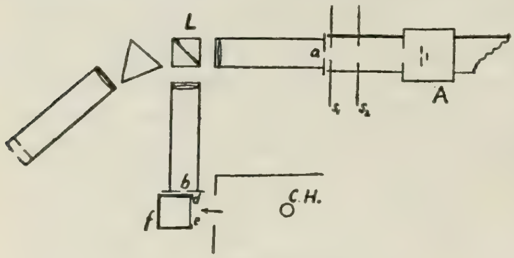

Fig. 175.

The three substances selected for measurements were fluorescein in aqueous solution slightly alkaline, eosin in alcohol, and resorufin in alcohol.

The solutions in each case were as dilute as was found practicable, so as to reduce the correction for absorption to a minimum.

In the determination of the fluorescence curves the solution was placed in a rectangular cell of white glass (*f*, Fig. 175) and was excited by the light from a Cooper-Hewitt mercury lamp, *C. H.* The tube of this lamp was vertical and mounted at a distance of about 30 cm. from the wall of the cell. Only those portions of the tube were used which were nearly in the same horizontal plane as the cell. The beam of exciting light entered the cell *f*, Fig. 175, in the direction of the arrow at right angles to the axis of the collimator.

The cell was inclosed within a metal box with black, matte, oxidized surfaces, and having only the broad rectangular opening *de* for the admission of the exciting light and a narrow, vertical, slit-like aperture opposite the slit *b* through which the fluorescence was viewed.

The use of the mercury arc, with its almost complete absence of light in the region occupied by the fluorescence bands to be measured, afforded further protection against stray light. In the study of the fluorescein solution the additional precaution was taken of inserting a cell of ammonio-sulphate of copper in water between the lamp and the fluorescent liquid, thus cutting off the yellow and green lines of the arc almost completely. The mercury lamp was fed from a storage battery of 120 volts with suitable resistance in series, and under these conditions it furnished an exciting light of unexpected constancy, surpassing in this respect any other source of suitable character and sufficient intensity with which we have had experience.

The arrangement of the apparatus for determining the fluorescence spectra is shown in Fig. 175. The plan is similar to that used in comparing the acetylene flame with the black body; but the photometer track carrying the flame was mounted in line with collimator *a*, while the fluorescence cell was placed in front of slit *b*. In the figure, *A* is the comparison flame; s_1 and s_2 are screens to prevent stray light from entering slit *a*; *f* is the cell of fluorescent liquid, and *C. H.* is the Cooper-Hewitt mercury arc lamp.

The procedure was as follows:

Slits *a* and *b* were set at equal widths of 50 divisions = 0.05 cm. The comparison flame was then moved up to a point on the track just in front of the aperture in screen s_2. The observing telescope was set for that region of the spectrum corresponding with the maximum of the fluorescence band to be measured. The fluorescent solution in cell *f* was diluted until its spectrum for that region was slightly stronger than the corresponding region in the spectrum of the comparison flame. By slightly shifting the observing telescope in either direction two places could now be found, lying a short distance from the crest of the fluorescence band, at which the two spectra were of equal brightness. The circle readings of these positions were noted, and the position of the comparison flame was read upon the scale of the photometer track. The flame was then moved to a slightly greater distance from slit *a*, and two new positions were found for the observing telescope, corresponding to points of equal brightness of the band farther from the crest. In this way the entire band was explored several times, and from these sets of readings the intensity of the band at various wave-lengths was computed in terms of the corresponding intensities of the spectrum of the acetylene flame.

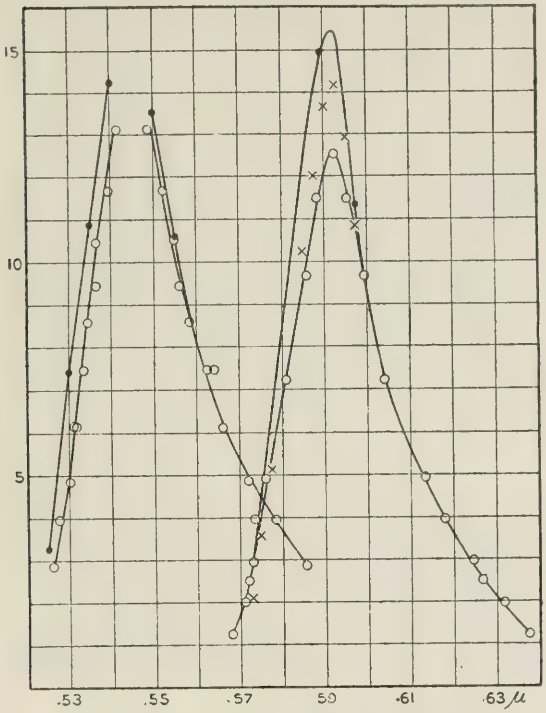

Fig. 176.—Eosin (to left) and resorufin.
The observed points are marked by circles.

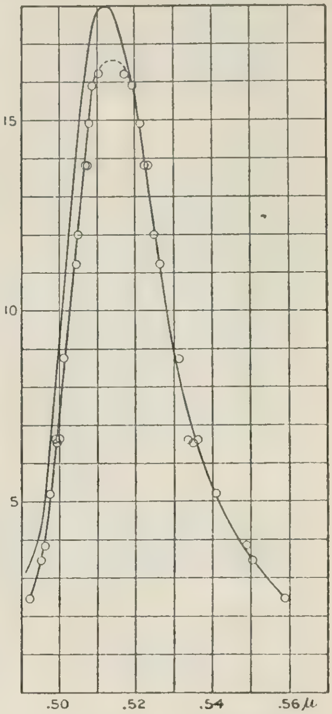

Fig. 177.—Fluorescein.
The observed points are marked by circles.

From these values the observed curves in Figs. 176 and 177 were plotted. The observed points are indicated by circles. The crosses and dots in this figure refer to corrected values referred to in a subsequent paragraph. In the case of eosin the wave-length of the crest is nearly the same as that of the green mercury line. Measurements in the region of the crest were therefore rendered uncertain by the presence of stray light from the green line. For this reason all the measurements in this region have been discarded. Observations near the crest of the fluorescein curve were also somewhat discordant, so that we do not regard this part of the curve as determined with much accuracy.

To obtain from the observed curves the distribution of energy in the fluorescence spectra it was necessary to make corrections for slit-width and absorption, and to multiply the ordinates of each corrected curve by the ordinates of the same wave-length in the curve giving the distribution of energy in the spectrum of the acetylene flame.

THE CORRECTION FOR SLIT WIDTH.

In the spectrophotometric comparison of sources of light having continuous spectra and nearly the same luminosity curves the correction for slit width disappears; but in the case of spectra consisting of narrow bands this is far from being the case. The slit-width correction used in the determination of the energy curves of incandescent solids does not apply, partly because it is the luminosity of the rays rather than their energy that is important, and partly because the distribution of luminosity in *two* sources has to be considered. The slit correction applicable to the Lummer-Brodhun spectrophotometer may be derived as follows: Let the luminosity curve of the source S_1, in front of the slit A, have the equation

$$L_1 = f(\lambda)$$

when the distance of the source is such as to give the standard intensity, which we shall call unity. If the distance is varied so that the intensity becomes i, then (λ being the wave-length)

$$L_1 = if(\lambda)$$

The luminosity of the source S_2 in front of the slit B will then be given by the equation

$$L_2 = rf(\lambda)$$

where r is the ratio of the energy of S_2 at the wave-length λ to the energy of S_1 at the same wave-length. r is itself a function of λ unless the two sources are identical in quality.

Images of the slit A are formed in the focal plane of the telescope for each wave-length of the spectrum of S_1. If the spectrum is continuous, we therefore have a series of overlapping images, forming a spectrum of greater or less impurity according to the width of the slit A.

The light reaching the eye from the slit A will depend upon the width of A, being proportional to this width if other conditions remain constant But it will also depend upon the width of the aperture C at the principal focus of the telescope, through which aperture the light used in making the setting must pass. If the spectrophotometer is used without an eye-piece, so as to obtain the benefit of the contrast field formed by the Lummer-Brodhun cube, all the light passing through C is used in illuminating the field, and the color is that resulting from mixing all the wave-lengths present. When the instrument is set to a match we therefore have equality between the total luminosity of the rays passing through C from A, and the total luminosity of the rays passing through C from B.

An expression for the total luminosity of the rays from A may be found as follows:

Let MN (Fig. 178) be the aperture at the focus of the telescope. It will be convenient to express the width $2c$ of this aperture in terms of wave-length. $2c$ is therefore not a constant, even if the actual width of the aperture is invariable, but depends upon the dispersion in the region of the spectrum where the observations are made. The widths of the slits A and B, denoted by $2a$ and $2b$, respectively, will also be expressed in terms of wave-length. We shall consider first the case where $a<c$.

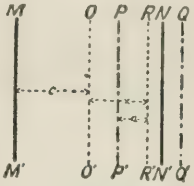

Fig. 178.

Let the center of C (OO' in the diagram) correspond to the wave-length λ. That image of the slit A which is formed by light of wave-length λ will have its center coincident with the center of the aperture. The image formed by light of wave-length $\lambda+x$ will be displaced by the distance x, so that its central line falls at RR'. For values of x lying between $+(c-a)$ and $-(c-a)$ all of the light forming the image of a will pass through the aperture. The total luminosity reaching the eye from such images will therefore be

$$L_1=\frac{2am}{d_1^2}\int_{-(c-a)}^{+(c-a)} f(\lambda+x)dx=\frac{2am}{d_1^2}\int_0^{c-a}\{f(\lambda+x)+f(\lambda-x)\}dx$$

where d_1 is the distance of the source S_1 from the slit and m is a factor, depending upon the dispersion of the prism, such that ma is proportional to the width of the slit in scale divisions. It is clear that $2am/d^2$ measures the intensity of the light entering the slit, the intensity being unity when the source is at unit distance and the slit width one division.

For values of x lying between $c-a$ and $c+a$ only a part of the image will be transmitted, the transmitted fraction being

$$1-\frac{x+a-c}{2a}$$

The total transmitted luminosity from these images that are partially transmitted will therefore be

$$\frac{2am}{d^2}\int_{c-a}^{c+a}\left(1-\frac{x+a-c}{2a}\right)\{f(\lambda+x)+f(\lambda-x)\}dx$$

$$=\frac{2am}{d_2}\int_{c-a}^{c+a}\left\{\frac{a+c}{2a}-\frac{x}{2a}\right\}\{f(\lambda+x)+f(\lambda-x)\}dx$$

Upon expanding $f(\lambda+x)$ and $f(\lambda-x)$ we have

$$f(\lambda+x)+f(\lambda-x)=f(\lambda)+xf'(\lambda)+\frac{x^2f''}{2}(\lambda)+\ldots+f(\lambda)-xf'(\lambda)+\frac{x^2f''}{2}(\lambda)-\ldots$$

$$=2f(\lambda)+x^2f''(\lambda)+\ldots$$

For any ordinary case the terms in higher powers of x may be neglected

The two integrals therefore become

$$\int_0^{c-a} \{ f(\lambda+x)+f(\lambda-x) \} \, dx = \int_0^{c-a} [2f(\lambda)+x^2 f''(\lambda)] \, dx$$

$$= 2\,(c-a)\,f + \frac{(c-a)^3}{3} f''$$

and

$$\int_{c-a}^{c+a} \left[\frac{c+a}{2a} - \frac{x}{2a} \right] [2f+x^2 f''] \, dx = \frac{c+a}{2a} \left[4af + \frac{(c+a)^3-(c-a)^3}{3} f'' \right]$$

$$- \frac{1}{2a} \left[\{(c+a)^2-(c-a)^2\} f + \frac{(c+a)^4-(c-a)^4}{4} f'' \right]$$

where f and f'' are written for $f(\lambda)$ and $f''(\lambda)$ respectively.

Upon adding the two integrals and introducing the factor am/d_1^2 we have

$$L_1 = \frac{2ma}{d_1^2} \left[2cf + \frac{c(a^2+c^2)}{3} f'' \right] = \frac{2ma}{d_1^2} [2cf+k_1 f'']$$

where

$$k_1 = \frac{c(a^2+c^2)}{3}$$

The form of the expression may be shown to be the same when $a<c$. Similarly for that portion of the field which is illuminated by S_2

$$L_2 = \frac{2mb}{d_2^2} \left[2crf + k_2 \left(\frac{\partial}{\partial\lambda} \right)^2 (rf) \right]$$

When the two fields are set to equality we have therefore

$$\frac{2ma}{d_1^2} \left[2cf+k_1 f'' \right] = \frac{2mb}{d_2^2} \left[2crf + k_2 \frac{\partial^2(rf)}{\partial\lambda^2} \right]$$

Expanding $\partial^2(rf)/\partial\lambda^2$ and remembering that the second term in the bracket is in each case small we have:

$$\frac{d_2^2\,a}{d_1^2\,b} \left[1 + \frac{k_1 f''}{2cf} \right] = r \left[1 + \frac{k_2}{2crf} (r''f+2r'f'+rf'') \right]$$

$$r = \frac{d_2^2 a}{d_1^2 b} \left[1 + \frac{k_1 - k_2'' f}{2cf} - \frac{k_2 r' f'}{crf} - \frac{k_2 r''}{2cr} \right]$$

An approximate value of r, usually a close approximation, is obtained by neglecting all terms after the first. This approximate value having been plotted as a function of λ, r' and r'' may be determined; and since f' and f'' may be obtained from the luminosity curve of the source A, the correction terms in the above expression can readily be computed.

In the experiments described in this paper the conditions were so chosen as to make $a=b=c$. In this case the expression for r becomes

$$r = \frac{d_2^2}{d_1^2} \left[1 - \frac{a^2}{3} \cdot \frac{r''}{r} - \frac{2a^2 r' f'}{3rf} \right]$$

If Δr is the increase in r which results from changing the wave-length from λ to $\lambda+2a$, and if Δf is the corresponding increase in f, we have approximately:

$$r' = \Delta r/2a, \quad f' = \Delta f/2a$$

For purposes of graphical computation we may conveniently express the approximate value of r'' in terms of the distance DC, Fig. 179. If this distance be called δr it may be readily shown that
$r''=2\delta/a^2$,

$$\therefore r=\frac{d_1^2}{d_2^2}\left[1-\frac{2\delta r}{3r}-\frac{1\Delta r\Delta f}{6rf}\right]$$

In computing these correction terms the luminosity curve given by Tufts was used.[1] The values of Δr and δr were taken from the curve showing the relation between λ and the approximate value of r.

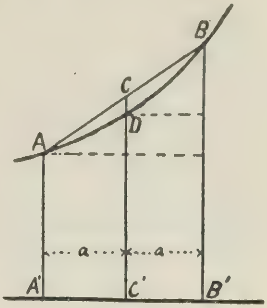

Fig. 179.

The correction depending upon δr is important only when the curvature of the r curve is considerable. In the present instance this correction is large for regions near the crest of the curve, but insignificant elsewhere. The importance of the correction is well shown in the curves for resorufin (Fig. 176), where the points marked with crosses show the curve after the slit correction has been applied. In the case of eosin and fluorescein the region near the crest was uncertain for the reasons already mentioned (p), so that the slit correction has not been applied in this region.

The second correction term, depending upon the product $\Delta r\Delta f$, is negligible near the crest of the luminosity curve of the source, where Δf is small. The term is thus of no significance in the case of eosin and fluorescein. Even with resorufin, where the whole luminescence spectrum lies well to the infra side of the crest of the luminosity curve, this correction is important only on the steep side of the curve. The result of applying the correction is shown by the points in Figs. 176 and 177 that are marked with crosses.

THE CORRECTION FOR ABSORPTION.[2]

The fluorescent light which enters the slit of the spectrophotometer in the foregoing experiments comes from a layer of liquid in the fluorescence cell having a thickness determined by the opening de, Fig. 175, through which the exciting light enters the cell. This layer, which is to be considered as uniformly fluorescent, extends from $x=x_1$ to $x=x_2$, where x is the distance from any point from which fluorescent light emanates to the wall of the cell in the direction toward the slit of the spectrophotometer.

Let the intensity of light, of any wave-length λ, sent toward the slit from the unit layer be i, and from a layer of thickness dx, be idx. If the coefficient of absorption of the liquid be α the light reaching the slit from the layer dx is $idxe^{-\alpha x}$ and the total intensity of light reaching the slit from the whole of the excited layer is

$$I=i\int_{x_1}^{x_2}e^{-\alpha x}dx=\frac{i}{\alpha}[e^{-\alpha x^1}-e^{-\alpha x_2}]$$

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[1] Tufts's curve (see Physical Review, XXIV, p. 433) was obtained for an incandescent light. But the difference between the color of the acetylene flame and that of the glow lamp in the region considered is so small that the error introduced is quite inappreciable.

[2] For a full description of the methods employed in determining the absorption of such solutions see Chapter XIII.

In the cell used in these determinations x_2 was 36.5 mm. and x_1 was 2.5 mm.

The coefficient a was determined by measuring the transmission of a cell containing a sufficient thickness of the fluorescent liquid to reduce the intensity of light of the wave-length of the middle of the absorption band to about 40 per cent. The correction for the losses of light in the glass and the solvent was determined by measuring transmission through the same cell when filled with absolute alcohol (or in case of fluorescein with water).

The correction for absorption, like that for slit-width, is of importance only in certain regions. The form of the fluorescence curves after the application of both corrections is shown in Figs. 176 and 177.

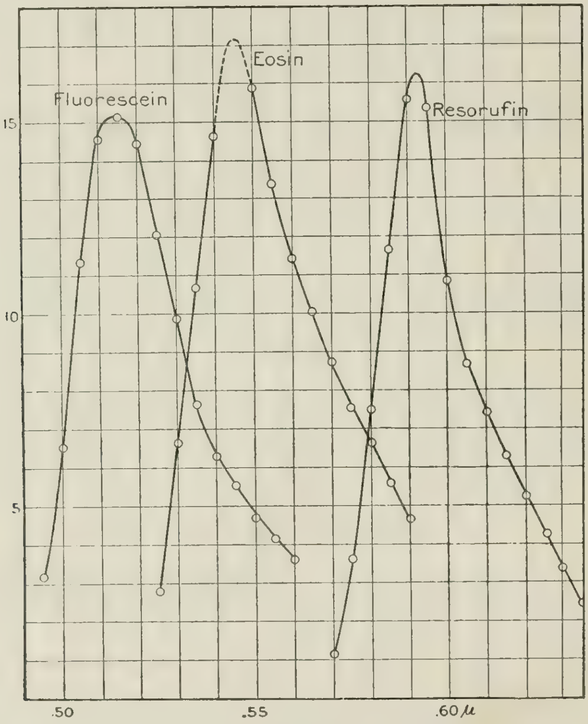

Fig. 180.

THE ENERGY CURVES OF FLUORESCENCE.

From the data corrected in the manner indicated in the two preceding sections curves for the distribution of energy in the fluorescence spectrum of the three substances under investigation were derived by multiplying each ordinate of the corrected curves of Figs. 176 and 177 by the ordinate of same wave-length in the energy curve of the acetylene standard (Fig. 173).

The resulting curves are given in Fig. 180. They suggest by their form a close resemblance between black-body radiation and fluorescence, excepting that the range of wave-lengths in the latter case is much smaller. Attempts to find some simply modified form of Wien's equation which will represent the results have thus far been unsuccessful.

CHAPTER XIII.

THE SPECIFIC EXCITING POWER OF THE DIFFERENT WAVE-LENGTHS OF THE VISIBLE SPECTRUM IN THE CASE OF THE FLUORESCENCE OF EOSIN AND RESORUFIN.

In the case of either a solid, like anthracene, or of a liquid such as one of the fluorescent dyes, fluorescence may usually be excited by light of a great variety of different wave-lengths. In fluorescent solutions there is commonly a well-marked absorption band lying close to the fluorescence band on the side toward the violet, and light of any wave-length within the limits of this absorption band will excite fluorescence. In fact fluorescence may usually be excited by light of much shorter wave-length, so that the solution will be lighted up when exposed to an ultra-violet spectrum. Simple inspection, however, is sufficient to show that the intensity of the fluorescence excited by various portions of a given exciting spectrum is widely different. It is not clear whether this variation is due to the fact that certain wave-lengths are particularly effective in exciting fluorescence, or whether it results merely from the fact that the absorbing power of the material varies for different wave-lengths. It is clear that light can not produce excitation unless it is absorbed by the fluorescent solution. Differences in absorbing power might therefore produce wide variations in the apparent effectiveness of different spectral regions in producing fluorescence, even if the specific exciting power, *i. e.*, the fluorescence excited per unit of *absorbed* energy, were in reality constant for all wave-lengths.

The determination of the relation between the specific exciting power and the wave-length of the exciting light is a problem of some interest, whose results possess also considerable significance on account of their bearing upon the theory of fluorescence. The present chapter deals with the determination of this relation for eosin and resorufin.[1]

The exciting light was furnished by a Nernst glower which took the place of the slit of a large spectrometer. A narrow region in the spectrum thus formed was used in exciting the solution studied, and the intensity of fluorescence produced was measured by a spectrophotometer as the wave-length of the exciting band was varied.

The arrangement for exciting and observing fluorescence will be made more clear by inspection of Fig. 181. The light of the Nernst glower, after passing through the large spectrometer before mentioned, was reflected directly upward by a total reflecting prism as shown in the figure, and passed through a horizontal slit S into the cubical glass vessel which contained the solution to be studied. The spectrometer was adjusted so as to bring the spectrum in focus at the slit S. One vertical face of the cubical cell was covered with a sheet of metal containing a slit S' as shown in the figure. The exciting light passing through the slit S excited a narrow vertical

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[1] An account of the experiments described in this chapter was given in the Physical Review, XXXI, p. 376, and p. 381, 1910.

strip in the liquid to fluorescence, and this was observed through the slit S', in front of which the collimator slit of the spectrophotometer was placed. The comparison source for the spectrophotometer, as in various experiments described in previous chapters, was an acetylene flame sliding upon a photometer track so that it could be set at different distances from the ground glass in front of the slit. This procedure makes it possible to keep the slit width constant and therefore eliminates the errors which might be introduced in measurements where the variation of intensity is great. The collimator slit of the spectrophotometer was broad and the instrument was set so as to measure the central part of the fluorescence band.

The Nernst glower which furnished the exciting light was attached permanently to the collimator tube of the large spectrometer. The wave-length of the light used for excitation was varied by swinging the arm carrying the collimator and glower, the other portions of the spectrometer remaining fixed in position. At frequent intervals, corresponding to wave-lengths of the exciting light which differed only slightly from one another, the intensity of the fluorescence excited was measured by the spectrophotometer. The cell containing the fluorescent solution was then emptied and carefully cleaned and a piece of magnesium carbonate was mounted obliquely in the cell so as to reflect light from the slit S into the spectrophotometer. The intensity and range of wave-lengths of the light thus reflected were measured for each of the spectrometer settings previously used. Finally the absorption of a layer of the solution of known thickness was measured for some definite wave-length in the spectrum. By a separate series of measurements the relative reflecting power of the magnesium carbonate was determined throughout the region used.

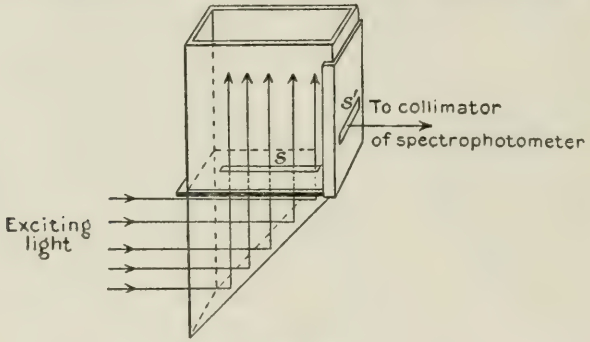

Fig. 181.

The procedure in computing results was as follows: To correct for the unequal reflecting power of magnesium carbonate at different wave-lengths the observed intensity, I_0, of the exciting light was divided by the reflecting power of magnesium carbonate for that particular wave-length. This correction reached approximately 10 per cent as its highest value. Using the values contained in Chapter XII for the distribution of energy in the spectrum of the acetylene flame, we next determined the relative energy of the light used for excitation as a function of the wave-length. It will be noticed that this procedure not only takes account of the difference in quality and energy distribution between the Nernst glower and the acetylene flame, but also eliminates any errors which might arise on account of selective transmission or other causes anywhere in the apparatus.

The center of the slit S' through which the fluorescence was absorbed was 8.2 mm. above the bottom of the cell containing the solution. On the average, therefore, the exciting light had passed through 8.2 mm. of solution before reaching the region whose fluorescence was measured by the spectrophotometer. The light available at this point to produce excitation was therefore less than that falling upon the face of the cell in the ratio of one to $e^{-0.82a}$. It was therefore necessary to compute this factor $e^{-0.82a}$ for each wave-length and for this purpose we determined with considerable accuracy the coefficient of absorption of both eosin and resorufin for different wave-lengths.

COEFFICIENTS OF ABSORPTION.

The measurements, which were extended throughout the absorption band for both dilute and relatively concentrated solutions of both substances, were made by comparing the intensity of the light transmitted by a cell containing pure alcohol with the transmission, for the same wave-length, when the cell was filled with the solution in question. For the concentrated solution two cells were used, the thickness of the absorbing layer being 1 cm. in one case and 3 cm. in the other. The dilute solutions were contained in a cell which gave an absorbing layer 29.5 cm. thick. The source of light for transmission was an acetylene flame. The comparison standard was also an acetylene flame, which was mounted so as to slide upon a track as previously described.

The ratio of the intensity of the light transmitted by the solution to the intensity of the light transmitted by the alcohol gave the percentage transmission, from which, with the thickness of the cell, the coefficient of absorption, a, could be computed, a being defined by the expression

$$I = I_0 e^{-ax}$$

where x is the thickness.

The results for eosin are shown in Fig. 182 and for resorufin in Fig. 183. Curve *I* in each case gives the coefficient of absorption for the dilute solution as a function of the wave-length, while curve *II* gives the coefficient of absorption for the concentrated solution. In Fig. 182 the scale is fifty times greater for curve *I* than for curve *II*, and in Fig. 183 the scale for curve *I* is ten times as large as that for curve *II*.

It will be seen that the absorption curve has very nearly the same form for the dilute and concentrated solutions. This is especially true in the case of resorufin, where each little ripple on the curve for the dilute solution is reproduced on the curve for the concentrated solution. In Table 25 will be found the values of a for the two solutions, together with the ratio of the two values. It will be seen that the ratio remains nearly constant throughout the whole spectrum. The variation from constancy is most marked at the two ends of the spectrum where the liability to experimental error is greatest. The results in the case of resorufin appear to indicate that the form of the absorption curve is not altered by concentration throughout the range studied and are thus in agreement with the results of Miss Wick.[1]

The appearance of the curve for resorufin suggests that the band is complex and that in addition to the principal maximum at 0.577 μ there are secondary maxima of absorption at about 0.558 μ and 0.536 μ. If the absorption of resorufin really consists of three overlapping bands, as seems probable, our results indicate that all three of these bands are produced by the ions.

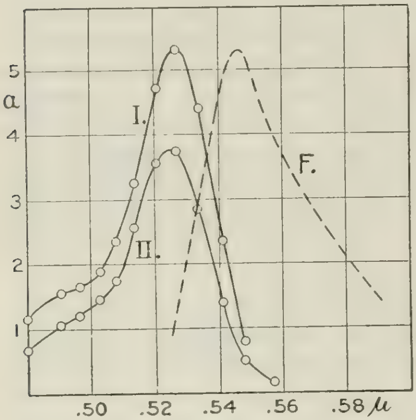

Fig. 182.—Eosin.

Curve *I* shows the coefficient of absorption as a function of the wave-length for a dilute solution. Curve *II* shows the same thing in the case of a concentrated solution. (The vertical scale in curve *I* is fifty times greater than that of curve *II*.) Curve *F* shows the distribution of energy in the fluorescence spectrum of fluorescein.

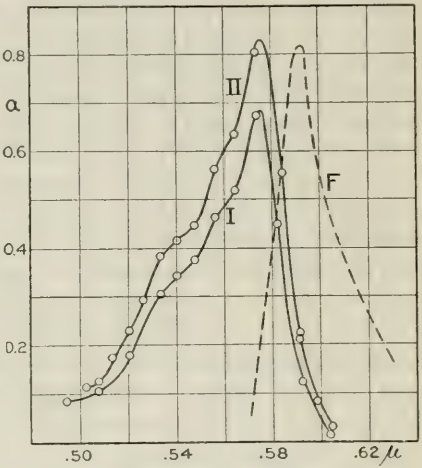

Fig. 183.—Resorufin.

Curve *I*, coefficient of absorption for dilute solution; curve *II*, coefficient of absorption for concentrated solution. (The scale of curve *I* is ten times greater than that of curve *II*.) Curve *II* shows the energy distribution in the fluorescence spectrum.

TABLE 25.

Coefficients of absorption for resorufin.

λ	α_1 Dilute.	α_2 Concentrated.	Ratio, $\alpha_2 : \alpha_1$
0.497μ	0.0078	....	....
.503	....	0.112	....
.508	.0107	.125	11.7
.514	....	.175	....
.521	.0180	.232	12.9
.527	....	.299	....
.534	.0307	.385	12.6
.541	.0349	.414	11.8
.548	.0372	.448	12.0
.557	.0467	.563	12.0
.565	.0522	.637	12.2
.574	.0674	.807	12.0
.583	.0448	.576	12.8
.585	....	.557	....
.593	.0126	.162	12.9
.599	....	.084	....
.604	.0017	....	....
.605	....	.032	....

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[1] Frances G. Wick, Physical Review, xxiv, p. 356; see also Chapter II.

In the case of eosin there is some indication of a secondary maximum in the neighborhood of 0.49 μ. The values of α for the two solutions and the ratios for these two values are given in Table 26. It will be noticed that the ratio is not nearly so constant as in the case of resorufin. There is perhaps some slight indication that the secondary band at 0.49 μ changes with the concentration at a different rate from the principal band, but it is doubtful whether the results are sufficiently accurate to give any certainty to such a conclusion. The small values of the ratio on the red side of the band imply a slight shift toward the red in the case of the dilute solution, but the region in which these small values in the ratio occur is the region where the results are most liable to error.

In each case we have shown by the curve *F* the distribution of energy in the fluorescence spectrum of the substance in question. The resemblance is noticeable between this curve of energy distribution and the absorption curve. Roughly speaking the one curve is the image of the other. In the absorption curve the side toward the red is steep, while the absorption dies away gradually toward the violet. In the fluorescence curve the intensity dies away gradually toward the red and stops abruptly on the violet side. When the mechanism of fluorescence is more fully understood the reason for this peculiar relationship between the two curves, which seems to be a characteristic of the fluorescent substances of this class, will doubtless be clear.

TABLE 26.

Coefficients of absorption of eosin.

λ	α_1 Dilute.	α_2 Concentrated.	Ratio, $\alpha_2 : \alpha_1$
0.480 μ	0.0116	0.356	30.7
.491	.0153	.540	35.3
.497	.0166	.597	35.9
.503	.0192	.736	38.3
.508	.0233	.870	37.2
.514	.0328	1.274	38.7
.521	.0473	1.765	37.3
.527	.0533	1.892	35.6
.535	.0444	1.422	32.0
.541	.0235	0.715	30.3
.548	.0083	.250	30.1

COMPUTATION OF SPECIFIC EXCITING POWER.

In the determination of the specific exciting power for eosin the solution used was the same as that employed in determining the absorption curve, for the more concentrated of the two solutions, shown in Fig. 182. The value of α for each wave-length could therefore be read off at once from that curve.

In the case of resorufin a different solution was used. Since, however, the form of the absorption curve is the same for all concentrations, it was sufficient to determine the absorption for one particular wave-length and then to reduce the values read from the curve for that substance (Fig. 183) in a constant ratio.

Having computed in this way the intensity of the rays which actually reach the region in the solution under observation, and which are therefore available for producing excitation, it was only necessary to find the amount of energy absorbed in each case by multiplying $I_0e^{-0.82a}$ by a. Finally the absorbed fluorescence, divided by the absorbed energy which produced it, gave the quantity sought, that is, *the intensity of fluorescence excited by unit quantity of absorbed energy of the particular wave-length in question.*

In the case of eosin the observed data, as well as the derived quantities corresponding to several steps in the computation, are given in Table 27. In the case of resorufin the same thing is shown graphically (Fig. 184). The observed points in each case are connected by full lines, while in the case of computed values the points are connected by broken lines. In curve *I* we have the intensity of the exciting light after reflection from magnesium carbonate. Curve *II* gives the intensity of the light actually reaching that part of the solution opposite the slit *S′*. The ordinates of curve *III* are obtained by multiplying each of the ordinates of curve *II* by a. Curve *III* therefore gives the energy actually observed from the exciting light for each wave-length. When the ordinates of curve *IV*, which shows the observed fluorescence, are divided by the ordinates of curve *III* we have the quantity desired, namely, the fluorescence excited per unit of observed energy (curve *V*).

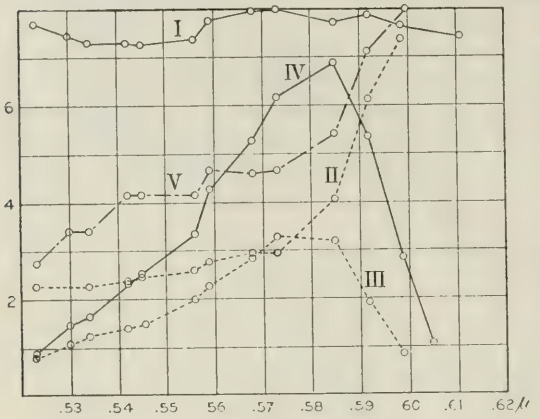

Fig. 184.
Resorufin.

TABLE 27.—Eosin.

1 λ	2 Intensity of fluorescence.	3 Intensity of exciting light.	4 Reflecting power of $MgCO_3$	5 I_0 corrected for reflection.	6 Energy in C_2H_2 spectrum.	7 I_0 (Energy.)	8 I_0e^{-ax}	9 aI_0e^{-ax}	10 Specific exciting power.
0.479μ	2.2	8.25	102	8.08	1.15	9.3	7.0	2.45	0.9
.485	2.9	8.4	103	8.15	1.38	11.2	7.67	3.53	0.82
.491	4.1	8.3	104	7.98	1.59	12.7	8.4	4.24	0.97
.497	5.3	8.4	105	8.00	1.77	14.2	8.65	5.20	1.02
.501	6.3	10.1	108	9.37	1.90	17.8	10.1	6.98	.90
.509	8.6	8.9	111	8.00	2.13	17.1	8.12	7.37	1.17
.514	10.4	11.2	111	10.1	2.26	22.8	8.13	10.3	1.01
.521	11.0	11.0	111	9.9	2.40	23.8	5.60	9.9	1.11
.526	13.0	12.2	111	11.0	2.58	28.4	5.98	11.4	1.14
.534	17.0	12.0	110	10.8	2.90	31.3	9.76	13.8	1.23
.540	18.3	12.5	109	11.5	3.14	36.2	19.6	14.7	1.25
.547	11.0	12.2	108	11.3	3.4	38.4	31.0	8.07	1.37
.556	4.8	12.7	107	11.9	3.84	84.5	42.7	3.85	1.25

The results for eosin are shown in Fig. 185 and for resorufin in Fig. 186. In the case of the latter figure the values corresponding to those shown in Fig. 184 are marked by circles. The crosses show the values obtained by another set of observations which are not here recorded in detail. The individual points on these curves show considerable erratic variation. In many cases these can be traced back to irregularities in the original data, doubtless due to some experimental errors. In making computations we have made no effort to eliminate these errors by smoothing the curves, but have taken each observation as it stood and carried through the work to the final result. Smooth curves have, however, been drawn among the computed points. The data and results recorded here represent the best of a number of series of observations. While those not recorded gave more irregular results than here shown they all agreed in indicating the same general trend in the final curve.

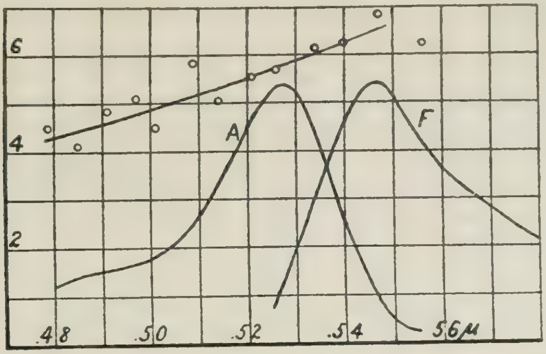

Fig. 185.—Eosin.

Intensity of fluorescence excited per unit of absorbed energy of different wave-lengths. Curve *A* gives the coefficient of absorption and curve *F* the energy distributed in the fluorescence spectrum.

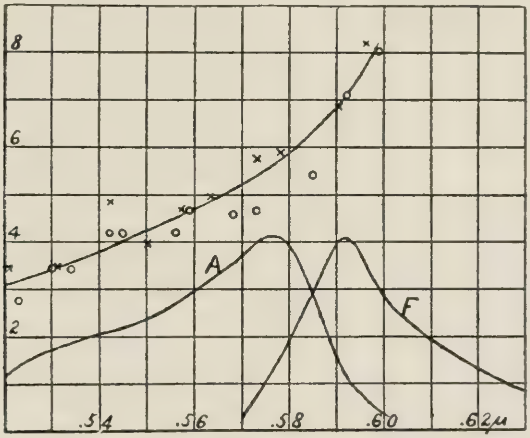

Fig. 186.—Resorufin.

Intensity of fluorescence excited by different wave-lengths per unit of absorbed energy. The circles and crosses give the results of two independent sets of observations. Curve *A* gives the coefficient of absorption and curve *F* the energy distribution in the fluorescence spectrum.

In each of these two figures also we have plotted the curves for the coefficient of absorption (A) and for the energy distribution in the fluorescence spectrum (F). It would seem reasonable to expect that the curve of specific exciting power might show some peculiarities either in the region of maximum absorption or in that of most intense fluorescence. It appears, however, that nothing of this kind occurs.

Before beginning these experiments we were of the opinion that either the specific exciting power would prove to be constant, so that the same quantity of absorbed energy would produce the same fluorescence regardless of its wave-length, or else that the effectiveness of the exciting light would prove to be greater for the shorter wave-lengths. The readiness with which fluorescence is excited in the ultra-violet spectrum made the latter view seem plausible. As it turns out, neither of these views is in accord with the facts. We were unfortunately unable to extend the observations to the ultra-violet spectrum. It seems clear, however, that if we confine our attention to wave-lengths falling within the range of one absorption band the light lying near the red side of the band is more effective in producing fluorescence than that lying on the violet side, and the change in the specific exciting power as we pass through the band is steady, without any indication of anything selective in the neighborhood of the region of maximum absorption.

CHAPTER XIV.

THE THEORY OF WIEDEMANN AND SCHMIDT.

The most comprehensive theory of luminescence thus far proposed is undoubtedly that first suggested by E. Wiedemann[1] in 1889, and later modified and extended by Wiedemann and Schmidt.[2] According to this theory some chemical or physical change is produced in a luminescent substance during excitation, and the emission of light is an accompaniment of the more or less gradual restoration of the modified substance to its original condition. Thus, in the case of phosphorescence, it was suggested by Wiedemann that a portion of the active material was changed by the exciting light from the stable condition A into the unstable state B. Phosphorescence would then result from a gradual breaking down of the unstable compound.[3] Fluorescence may be due either to the vibrations set up during the change from A to B, or to the fact that the reaction $B \rightarrow A$ proceeds, with emission of light, during excitation as well as during decay. Thermo-luminescence is to be explained as the result of some chemical change produced by heat, during the progress of which the molecules are thrown into such violent vibrations as to bring about the emission of light. Luminescence ceases in such cases when the change has been completed; and some outside stimulus is required, such as that furnished by kathode rays, to restore the substance to the sensitive state. Not only is this explanation of thermo-luminescence a plausible one, but in several instances evidence has been found that the assumed change really occurs. In the paper already referred to, Wiedemann and Schmidt have discussed all of the various types of luminescence in considerable detail and have shown that the theory proposed by them will account for the phenomena, at least qualitatively, in a very satisfactory way.

It has generally been assumed that the change accompanying luminescence is of a chemical nature. Various suggestions have been made in regard to the character of the reactions produced by the exciting light (or other cause), and attempts are not lacking to trace a connection between luminescence and chemical constitution. It was pointed out, however, by Wiedemann and Schmidt that in many cases there were reasons for looking upon electrolytic dissociation as the more probable cause of luminescence. In fact, since the electromagnetic disturbance that constitutes light can get a hold on the molecules of the active material only by exerting forces upon the electrical charges in the molecule, and will always tend to separate the positive and negative parts, it appears probable that the first effect of the exciting light is *always* to produce some type of electrolytic dissociation, and that any chemical changes which may be exhibited are

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[1] E. Wiedemann, "Zur Mechanik des Leuchtens," Wied. Ann., 37, p. 177, 1889.

[2] E. Wiedemann, and C. C. Schmidt, Wied. Ann., 56, p. 177, 1895.

[3] E. Wiedemann, *l. c.*, pp. 224–225.

secondary effects.[1] But although the exciting light causes a separation of the active molecule into positive and negative parts, it appears unlikely that these parts are the ions of ordinary electrolysis. There are many substances like fluorescein and eosin which fluoresce only when dissociated. In such cases fluorescence can not be due to the recombination of ions; for dissociation and recombination are taking place in an electrolytic solution all the time, and if this were the cause of luminescence we should expect the solution to glow continuously without the action of any exciting light. Fluorescence in such cases must be due to some action upon the ions themselves. Now it can scarcely be doubted that the absorption of the exciting light is the result of resonance on the part of the molecules or atoms of the active substance; and although the vibrational energy thus imparted to the molecules is rapidly transformed by collisions into translational energy (heat), yet under favorable conditions the molecules might be thrown into such violent oscillation as to be torn apart. It seems, therefore, that the most plausible assumption to make is that the first effect of the exciting light is to produce such violent vibrations as to liberate one or more electrons from the molecule; in other words, to bring about dissociation similar to that produced by Roentgen rays. For the sake of definiteness we shall adopt this view in the discussion that follows.

Among the facts of luminescence that are satisfactorily accounted for by the theory of Wiedemann and Schmidt is the law that the distribution of intensity and the wave-length of maximum intensity for each band in a luminescence spectrum are independent of the mode of excitation.[2] Light corresponding to any part of the absorption band may, if sufficiently intense, produce dissociation; and dissociation may also be brought about by various other agencies, such as the action of Roentgen rays and kathode rays. But the manner in which recombination occurs, and therefore the form of the luminescence spectrum, will not depend in any way upon the manner in which the dissociation was produced.

The theory also leads directly to the conclusion that the light emitted during the luminescence of an isotropic substance is unpolarized, whatever may be the condition of polarization of the exciting light, and this conclusion is in agreement with the experimental results in all cases where polarization tests have been applied.

The law of Stokes that the light emitted during photo-luminescence is of greater wave-length than the exciting light has always proved a stumbling-block in the development of theories of luminescence, and at first glance the difficulty appears to be as great in the case of the Wiedemann and Schmidt theory as in any of the other theories proposed. Why should the vibrations that occur on recombination differ in period from those originally set up by the exciting light? It is indeed possible that the latter are forced vibrations, whose period bears no simple relation to the natural period of the molecule; but it is more reasonable to expect that vibrations which bring about actual disintegration are produced by resonance. If

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[1] It is to be observed that this reasoning does not apply to the case of kathodo-luminescence, since there is no reason why the kathode-ray bombardment should not directly cause chemical changes. The relatively great chemical activity of kathode-ray excitation as compared with excitation by light is probably connected with this essential difference in the mechanism of excitation in the two cases.

[2] This law, first proposed by Lommel in the case of photo-luminescence, has been tested by the writers for numerous cases of fluorescence excited by light of different wave-length (see Chapter I) and for several cases of excitation by kathode rays and Roentgen rays (see Chapter IX).

this is true we have to do with the natural period of the molecule in both cases, and it would seem that the light emitted during luminescence should have the same wave-length as the exciting light. In the discussion that follows we venture to make a suggestion which offers an explanation of this difficulty.

In the case of photo-luminescence in solids and liquids the active molecule is always closely surrounded by other molecules. In general these surrounding molecules belong to the solid or liquid solvent in which the active material is dissolved. If we have to deal with the luminescence of a pure substance (if such cases occur), the surrounding molecules are of the same kind as those which participate in the luminescence phenomena. But in either case the period of vibration will be different from what it would be if the vibrating molecules were isolated. Since the change in period will be relatively great for those molecules that are close to their neighbors and smaller for those that are farther away, it is seen that the natural period will vary through a considerable range as the active molecules move about, and at each instant there will exist in the substance molecules having all periods lying between certain rather wide limits. The absorption spectrum of the substance therefore consists of bands rather than of lines.[1]

When a molecule is dissociated by the action of the exciting light, the two parts, being electrically charged, will be more strongly attracted by the molecules of the solvent than was the original neutral molecule. Recombination of the separated ions is therefore more likely to occur when the latter are in the immediate neighborhood of the molecules of the solvent, *i. e.*, under conditions which make the period of the resulting vibrations longer, on the whole, than the period natural to the active molecules before dissociation. Since recombination can occur under a variety of conditions a wide range of wave-lengths will be represented in the luminescence spectrum; the latter also will consist of bands rather than of lines. But on the whole the wave-length of the light emitted during luminescence will be longer than that of the exciting light. The same sort of thing will occur, although in less marked degree, even when the active molecule is itself electrically charged, as in the case of fluorescein. In this case, as well as in that first considered, it may even be that each of the two parts into which the active molecule is dissociated becomes a nucleus to which neutral molecules are attracted, so that the ions become heavy aggregations of molecules. This is the assumption usually made regarding the production of ions in gases by the action of Roentgen rays, kathode rays, etc. If this is the real condition of affairs, the reasons for increased wave-length in the light emitted are still more evident.

It will be seen that this way of looking at the phenomena of photo-luminescence gives what might be called a mechanical explanation of Stokes's law. It does not lead us to expect, however, that Stokes's law will always be exactly followed. The luminescence spectrum and the absorption spectrum may overlap; in fact, it is to be anticipated that they will do so in the majority of cases. This is in agreement with the more recent experiments on this subject.

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[1] Essentially this explanation of the broadening of spectral lines has been discussed in some detail by Galitzin, Wied. Ann., 56, p. 78, 1895.

Upon the basis of the dissociation theory of luminescence it is clear also that we should expect no change in the form of the phosphorescence spectrum during decay.[1] The intensity of phosphorescence will depend at each instant upon the number of recombinations that occur per second, and will therefore diminish as the number of free ions becomes less. But it seems probable that the number of recombinations that occur under such conditions as to give light of a certain wave-length will still remain the same fraction of the whole number. The case has some resemblance to that of the distribution of velocities among the molecules of a gas; if the total number of molecules in a given volume is diminished, the number having a given velocity will also diminish; but this number will still be the same fraction of the whole.

Probably the most serious objection to the form of the theory of Wiedemann and Schmidt that is here considered is the absence of any direct evidence of electrolytic dissociation during the excitation of luminescence. The experiments of Howe,[2] although carried out with apparatus of high sensibility, fail to show any ionization in anthracene vapor when excited to fluorescence. Ionization of gases by the direct action of ultraviolet light has indeed been observed in numerous instances, but not under conditions which indicate any connection with luminescence. No change in electrical conductivity during excitation, such as might be expected to result from electrolytic dissociation, could be detected in fluorescent liquids by Cunningham, Regner, or Camichel. Our own experiments with alcoholic solutions of the fluorescent dyes seemed at first to indicate an increase in conductivity during fluorescence in some cases as great as 1 per cent. But the work of Hodge and of Goldman has shown that these results were in reality due to a change in polarization or to the establishment of a photo-electric E.M.F.[2]

On the other hand, Lenard has found indirect evidence of an increase in the conducting power of certain phosphorescent sulphides during luminescence. The fact that luminescent substances usually exhibit strong photoelectric activity, as was first pointed out by Elster and Geitel, also points to a close connection between ionization and luminescence. Even the absence of increased conductivity in fluorescent liquids is not so important as would at first appear, for the solutions tested were those in which the property of fluorescence resides in the ion. If a negative ion is dissociated by the separation of an electron no change in the number of ions will result, and the only change that could be expected in the conductivity is that which might come from a change in the mobility of the ions. Whether the mobility would be increased or decreased we have no means of telling; but that the change would not be great seems reasonably certain.

While the failure of experiments to detect increased conductivity in solutions thus appears to be without great significance, the fact that cells containing fluorescent liquids give an E.M.F., when one electrode is illuminated, which is far greater than that of other photo-active cells, gives another instance of a close connection between fluorescence and electrical effects.

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[1] The hypothesis of molecular groups developed in Chapter XV in discussing the form of the decay curve calls for a slight change in the form of the spectrum. But it seems probable that this change is so small as to be difficult of detection.

[2] See Chapter X.

It is to be remembered that the rays that produce photo-activity in such cases are the same that cause fluorescence. Goldman has further shown that the behavior of photo-active cells with fluorescent liquids is such as to indicate the liberation of negative electricity at the illuminated electrode at a constant rate depending upon the intensity of illumination. Goldman's results are thus in complete accord with the view that fluorescence is accompanied by ionization.

It appears, therefore, that while there is no *direct* evidence of electrolytic dissociation in fluorescent solids and liquids, many phenomena have been observed which make it seem probable that such dissociation exists. A detailed study of this very interesting class of phenomena is much to be desired, and will doubtless suggest some means by which a very fundamental question in the theory of luminescence may be definitely settled.

In the case of gases the experimental results are less favorable for the dissociation theory of luminescence, and in the case of fluorescence seem to directly contradict it. Before accepting these results, however, as conclusive evidence of the falsity of the theory, it is desirable to consider the nature of the differences which the theory would lead us to expect between the behavior of gases and liquids.

It can scarcely be doubted that in the case of liquids or solid solutions the presence of the solvent is favorable to the ionization of the solute. The solvent acts as a catalytic agent, both for ordinary dissociation and for that which we assume to be produced by light. To form a picture of the process by which this catalytic action is effected, let us consider a molecule of the solute (active substance in the case of luminescent substances) which is subjected to some influence tending to separate it into positive and negative parts. Such a tendency might result from a violent collision or from strong resonant vibrations set up by light. As soon as the separation begins it will be aided by the attraction of the neighboring neutral molecules of the solvent, and when dissociation has actually occurred the ions are rendered more sluggish in their movement, and are to some extent prevented from recombining, by becoming attached to the solvent molecules. If we imagine the solvent removed, so that we have to deal with a gas instead of a solution, it is readily seen that the conditions are less favorable to ionization for two reasons:

(1) The forces to be overcome in effecting dissociation are far greater, since there are no solvent molecules to partially counteract the mutual attraction of the ions; and for the same reason the ions must be driven much further apart in order that the separation may be complete;

(2) The tendency toward recombination is greatly increased, both because of the greater effective attractive forces between the ions and because of their more rapid motion.

It is not surprising, therefore, that spontaneous electrolytic dissociation is very rarely observed in gases. HCl in dilute solution is a good conductor. But the same amount of HCl in the form of a gas, occupying the same volume as before, shows no conducting power except such as requires the most refined apparatus for its detection. Does it not seem reasonable therefore that the ionization produced in a gas by light should also be very minute, so that we may hope to detect it only under especially favorable conditions, and by means of apparatus even more sensitive than that thus far used?

It may be also that some type of dissociation occurs in gases that is incapable of producing a change in electrical conductivity, but nevertheless as effective as complete dissociation in producing fluorescence. For the sake of definiteness let is assume that fluorescence is due to the vibrations of one ring of the Saturnian atom proposed by Sir J. J. Thomson. We can imagine this ring set into such violent vibration by light of suitable period that an electron is broken loose. This electron will later return and, by setting up vibrations when it reenters the ring formation, will cause fluorescence. But the separation of an electron from such a ring does not necessarily mean dissociation in the electrolytic sense. In order that complete dissociation should occur the electron must be driven away to such a distance as to be practically beyond the influence of the remainder of the atom. The energy required to accomplish this is probably far greater than that required to break down a ring; and complete dissociation, which alone can manifest itself by an increase in electrical conductivity, may be of relatively rare occurrence, even in cases of brilliant fluorescence. It may be pointed out in passing that the partial polarization observed by Wood in the light emitted by fluorescent sodium vapor is to be expected if the view outlined above regarding the nature of fluorescence in gases is accepted.

In the case of phosphorescent gases electrolytic dissociation is readily detected so long as phosphorescence lasts. In such cases the dissociation appears to be complete. The long duration of the after-glow in gases suggests that the ions attach themselves to neutral molecules and in consequence move slowly; and the fact that the spectrum often consists of bands rather than lines is in accord with this view. The decay of phosphorescence in gases follows the law that is predicted by the dissociation theory in its simplest form,[1] and seems to be almost entirely free from the disturbing influences present in the case of solids.

While we are by no means justified in looking upon the theory of Wiedemann and Schmidt as finally established, it appears to us, in the light of the preceding discussion, that it is by far the most promising of the theories thus far suggested, and that it affords a most useful guide in the experimental study of luminescence.

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[1] C. C. Trowbridge, Physical Review, vol. 26, p. 515, 1908; vol. 32, p. 129, 1911.

CHAPTER XV.

THE PHENOMENA OF PHOSPHORESCENCE CONSIDERED FROM THE STANDPOINT OF THE DISSOCIATION THEORY.

It is our purpose in this chapter (1) to derive the law of decay of phosphorescence which the dissociation theory would lead us to expect under such ideally simple conditions as seem to exist in the case of gases; and (2) to consider in turn the various modifying factors which may have an influence on the phenomena of phosphorescence in solids, and to determine so far as possible the nature of this influence. Comparison with experimental results will then make it possible to form an opinion of the relative importance of the various factors considered.

It will facilitate the discussion if we consider first the requirements which a satisfactory theory must meet. The most important experimental results in the case of photo-luminescence are briefly mentioned below:

SUMMARY OF EXPERIMENTAL LAWS.

1. Stokes's Law.
2. If we isolate a single band of the luminescence spectrum it is found that the distribution of intensity throughout the band is independent of the intensity and wave-length of the exciting light.
3. The light emitted by an isotropic substance during luminescence is unpolarized, no matter what may be the condition, as regards polarization, of the exciting light.
4. During the decay of phosphorescence each band of the luminescence spectrum behaves as a unit; *i. e.*, the wave-length of maximum intensity and the relative distribution of intensity throughout the band remain unchanged.

These general laws were discussed in the preceding chapter and it was pointed out that they are directly deducible from the dissociation theory.

To these four general laws must be added the following experimental facts connected with the decay of phosphorescence:

5. *Form of Decay Curve.* The curve obtained by plotting the values of $I^{-\frac{1}{2}}$ as ordinates and the corresponding values of t as abscissas is a straight line for small values of t; it changes to a curve concave toward the axis of t as t increases; but for still larger values of t the relation between $I^{-\frac{1}{2}}$ and t is again linear, and remains so until I becomes too small to measure. The form of the decay curve is dependent on the intensity and duration of excitation, the slant being altered in each of the straight parts by a change in either of these two factors in the excitation.
6. *Hysteresis.* The behavior of a phosphorescent substance with a given excitation depends upon its previous history. Some semi-permanent change is produced by excitation which persists for several hours, or even for several days, after visible phosphorescence has ceased.

7. *Effect of Red and Infra-red Rays.* In the case of certain substances the semi-permanent condition produced by excitation may be destroyed and the material restored to a standard state by a brief exposure to the red and infra-red rays. The effect of the longer waves during phosphorescence is to accelerate the decay. In some cases the first effect is to increase the brightness of phosphorescence, this temporary effect being followed by decay more rapid than the normal.

THE DECAY OF PHOSPHORESCENCE UNDER SIMPLE CONDITIONS.

According to the form of the Wiedemann and Schmidt theory that is here adopted, the effect of the exciting light is to produce electric dissociation of the active substance and the resulting negative and positive nuclei exist for a time uninfluenced by their mutual attraction. The vibrations that occur upon the recombination of the ions give rise to phosphorescence.

The simplest hypothesis regarding the law of recombination of the ions in a luminescent substance is that which has been applied to the case of ionization in gases.[1] Let the number of positive ions present per cubic centimeter at any time t be n. The number of collisions between a positive and a negative ion will be proportional both to the number of positive ions and to the number of negative ions; and a certain fraction of these collisions will result in recombination. Since positive and negative ions are present in equal numbers we have

$$dn/dt = -\alpha n^2 \qquad 1/n = c + \alpha t \text{ where } c = 1/n_0$$

Since the intensity of phosphorescence is proportional to the number of recombinations per second

$$I = k\alpha n^2 = k\alpha/(c+\alpha t)^2$$

This is one form of the empirical expression originally proposed by E. Becquerel to express the decay of long-time phosphorescence, and is the same law that was derived on the basis of entirely different theoretical assumptions by H. Becquerel.[2]

In comparing our experimental results with the law just derived, it is convenient to write the above expression in a different form, namely,

$$\frac{1}{\sqrt{I}} = a + bt$$

where

$$a = \frac{1}{n_0\sqrt{k\alpha}} \qquad b = \sqrt{\frac{\alpha}{k}}$$

The decay of phosphorescence in gases appears to be strictly in accordance with this law.[3] Under certain special conditions as regards temperature, etc., the law is very closely obeyed by zinc sulphide and even by Balmain's paint.[4] But in the great majority of instances the phosphores-

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[1] Rutherford, Philosophical Magazine, vol. 44, p. 422, 1897.

[2] H. Becquerel, Comptes Rendus, vol. 113, p. 618, 1891.

[3] C. C. Trowbridge, Physical Review, vol. 26, p. 515; vol. 32, p. 129.

[4] C. A. Pierce, Physical Review, vol. 26, p. 312 and p. 454, 1908. See also Chapter VI.

cence of solids decays in accordance with a more complicated law. As stated above, the curve obtained by plotting values of $I^{-\frac{1}{2}}$ as ordinates and the corresponding values of t as abscissas is not linear throughout, as the simple theory would lead us to expect. The curve is straight, both for small values of t and for large values of t, but shows a sharp curvature for intermediate values.

It has been suggested by H. Becquerel[1] that the form of curve observed in the case of solids is to be accounted for by assuming that the phosphorescence spectrum consists of two bands, each of which obeys the simple law, but having different rates of decay. If a decay curve is plotted for each of the two assumed bands the equations of the two curves will be

$$I_1^{-\frac{1}{2}} = a_1 + b_1 t \qquad I_2^{-\frac{1}{2}} = a_2 + b_2 t$$

and each of the two curves will be a straight line. But if we plot $I^{-\frac{1}{2}}$ against t, where I is the observed total intensity $(I = I_1 + I_2)$ the resulting curve will not be straight but will take the form shown by curve C, Fig. 187. In this figure A and B are the decay curves for the two bands taken separately. In the case represented in the figure the two bands are assumed to decay at widely different rates, and the band which decays more rapidly (A) has initially the greater intensity. It will be seen that under these circumstances the decay curve for total intensity has all the characteristics of the curves determined by experiment. Becquerel cites one substance for which the observed intensity can be represented by the expression

$$I = 1/(a_1 + b_1 t)^2 + 1/(a_2 + b_2 t)^2$$

with remarkable accuracy. In the case of this particular substance Becquerel also found independent evidence of the existence of two bands in the phosphorescence spectrum.

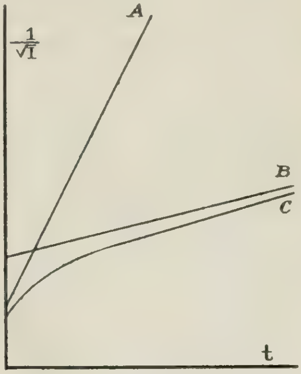

Fig. 187.

Illustrating Becquerel's explanation of the form of the decay curve in solids.

This way of accounting for the form of the decay curve was also proposed by Pierce in discussing the decay of phosphorescence in Emanationspulver, and has been shown by him to give a very satisfactory explanation of the change in the form of the decay curve resulting from changes in temperature.

If Becquerel's explanation of the form of the decay curve is correct we should expect to find a change in the phosphorescence spectrum during decay. For, referring to the figure, the light given out during the first few seconds is chiefly due to band A, while that emitted during the later stages of decay is almost entirely due to band B. Unless these two bands are coincident some shift in the wave-length of maximum intensity is to be expected. Our own experiments with Sidot blende show that no measurable change occurs in the form of the spectrum, or the position of its maximum, during the first 10 seconds, and the later work of Pierce shows that the wave-length of maximum intensity is unchanged for at least 1

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[1] Becquerel, *l. c.*

minute.[1] The results of Waggoner and Zeller with short-time phosphorescence, although less accurate, point to the same conclusion.

In the case of our own observations on Sidot blende we have expressed the opinion that the curves obtained are to be regarded as showing the decay of the green band alone; for although Sidot blende also possesses bands in the blue and violet, these decay so quickly and are of such small luminosity that they can scarcely affect the curves to any appreciable extent. In the later work of Werner[2] special precautions were taken in the choice of a substance and in the use of color screens to make certain that one band only was studied; yet the curves obtained are of exactly the same type as those found by other observers.

The work of Werner, even more strongly perhaps than the work of Pierce and our own work with Sidot blende, thus appears to discredit any explanation of the form of the decay curve that is based upon the assumption of two bands in the phosphorescence spectrum. It can not be denied, however, that two bands may well be present, even when special precautions of this kind are taken, and even when the spectrophotometer shows no indication of a double band. The bands of a phosphorescence spectrum are ordinarily so broad that two bands lying close together might readily appear as one. If the case is one where the bands actually overlap it would not be possible to make observations on one alone without working at the extreme edge of the double band, where the intensity would probably be too small to permit of accurate observations. An extremely small shift in the maximum might also fail of detection even by the photographic method of Pierce. It does not at present appear possible to devise a method of obtaining absolutely conclusive proof that Becquerel's explanation is not correct. Since the assumption of two nearly coincident bands offers so direct an explanation of the form of the decay curve, and since it seems certain that curves may be plotted on the basis of this assumption which deviate from the observed curves by less than the experimental errors, it must be admitted that the hypothesis has much in its favor.

There are several reasons, however, for looking upon this explanation of the form of the curve with suspicion. In the first place, it does not account either for the remarkable changes produced in the decay curves by varying the intensity and duration of excitation, or for the phenomena of hysteresis that have been observed in almost all cases of long-time phosphorescence. It also leaves untouched the question of the effects produced by exposure to the longer waves. An even more serious objection is the fact that it is necessary to assume the existence of two nearly coincident bands in all cases of long-time phosphorescence; for upon replotting the decay curves obtained by different observers with $I^{-\frac{1}{2}}$ and t as coordinates it is found that the curves are of the same type for all substances thus far tested. It is hardly credible that this is accidental. Only two explanations appear to be possible: either the existence of two nearly coincident bands is an essential characteristic of substances showing long-time phosphorescence, or else the peculiarities exhibited in the form of the decay

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[1] This result has recently been confirmed by H. E. Ives and M. Luckiesh (Astrophysical Journal, vol. XXXIV, p. 173, 1911), who find that the phosphorescence spectrum remains the same for at least fifteen minutes after the beginning of decay.

[2] A. Werner, Ann. der Phys., 24, p. 164, 1907.

curve are to be explained in some manner which does not involve the assumption of two bands at all. While it may prove of interest at some later time to develop the theory along the lines suggested by the first of these alternatives, the present discussion will be based upon the acceptance of the second, and we shall consider in what ways the form of the decay curve, as well as certain other peculiarities of phosphorescence, may be explained in substances possessing only one band in the phosphorescence spectrum.

ABSORPTION EFFECTS.

If a homogeneous substance possessing only one band in its phosphorescence spectrum is uniformly excited throughout, and if the light emitted by the interior portions suffers no diminution by absorption before reaching the surface, then according to the dissociation theory here considered the decay of phosphorescence will be in accordance with the law

$$\frac{1}{\sqrt{I}} = a + bt$$

These conditions, however, can never be exactly attained. The exciting light must be absorbed to some extent, for otherwise no energy would be available to produce phosphorescence. The excitation will therefore be greatest at the surface, and will diminish, at a rate determined by the absorbing power of the material, as we pass to points within. Since the ions are in consequence more numerous in the surface layers, and since the number of recombinations per second, which determines the intensity of phosphorescence, is proportional to the square of the number of ions, it is clear that the light emitted during the early stages of decay will come chiefly from the surface. As decay proceeds, however, the relatively high rate of recombination at points where n is large will cause a rapid approach to uniformity of ionic concentration, and the part contributed to the total light by the interior of the mass will become increasingly important. At first the intensity of phosphorescence is approximately proportional to $V_1 \alpha n^2$, where V_1 is the volume of the surface layer that is chiefly effective. Later, when the light from the interior becomes comparable in intensity with that from the surface, the phosphorescence will be approximately proportional to $V_2 \alpha n^2$, where $V_2 > V_1$. In terms of the total number of ions, N, the two intensities will thus be approximately proportional to $\alpha / V_1 \cdot N^2$ and $\alpha / V_2 \cdot N^2$. So far as the slant of the decay curve is concerned this is equivalent to a decrease in the coefficient of recombination and will result in making the curve concave toward the axis of t. Absorption of the emitted light will complicate the phenomena but will not modify the general result. The effect of absorption is therefore to produce a change in the form of the decay curve which is at least in the right direction to account for the observed deviation from linearity.

In discussing the effect of absorption in detail we shall assume that both the exciting light and the emitted light suffer absorption, the two coefficients of absorption being β and γ respectively. At any depth x below the surface the intensity of the exciting light will be

$$E = E_0 e^{-\beta x}$$

Assuming that ions are produced at a rate proportional to E and that excitation has proceeded for a sufficient time to produce a steady condition, the number of ions per cubic centimeter at any depth x will be determined by the equation

$$\frac{dn}{dt}=0=hE-\alpha n_0^2=hE_0e^{-\beta x}-\alpha n_0^3 \qquad n_0=\sqrt{\frac{hE_0}{\alpha}}\,e^{-\frac{1}{2}\beta x}$$

If n is the number of ions per cubic centimeter at the time t we have

$$n=\frac{1}{1/n_0+\alpha t}$$

and the light emitted per unit volume, denoted by i, is

$$i=p\alpha n^2=\frac{p\alpha}{(1/n_0+\alpha t)^2}$$

p being the light emitted as the result of one recombination.

Since the emitted light suffers absorption, the amount contributed to the total observed intensity by a layer of thickness dx will be

$$idxe^{-\gamma x}=\frac{p\alpha e^{-\gamma x}dx}{(1/n_0+\alpha t)^2}$$

and the total intensity is

$$I=p\alpha\int_0^{\infty}\frac{e^{-\gamma x}dx}{(ae^{\frac{1}{2}\beta x}+\alpha t)^2}=p\alpha\int_0^{\infty}\frac{e^{-\gamma x}e^{-\beta x}dx}{(a+\alpha te^{-\frac{1}{2}\beta x})^2}$$

where

$$a=\sqrt{\frac{\alpha}{hE_0}}$$

Putting

$$\alpha te^{-\beta x/2}=z$$

so that

$$dz=-\frac{\alpha\beta t}{2}e^{-\frac{\beta x}{2}}dx \quad\text{and}\quad e^{-\gamma x}=\left(\frac{z}{\alpha t}\right)^{\frac{2\gamma}{\beta}}$$

$$I=-\frac{2p\alpha}{\beta(\alpha t)^{m+2}}\int_{\alpha t}^{0}\frac{z^{m+1}dz}{(a+z)^2}$$

where $m=2\gamma/\beta$.

Successive partial integration gives

$$I=-\frac{2p\alpha}{\beta(\alpha t)^{m+2}}\left[\frac{1}{m+2}\frac{z^{m+2}}{(a+z)^2}+\frac{2}{m+2\cdot m+3}\frac{z^{m+3}}{(a+z)^3}\right.$$
$$\left.+\frac{2\cdot 3}{m+2\cdot m+3\cdot m+4}\frac{z^{m+4}}{(a+z)^4}+\dots\right]_{\alpha t}^{0}$$

Upon putting in the limits this becomes

$$I=\frac{2p\alpha}{(m+2)\beta}\cdot\frac{1}{(a+\alpha t)^2}\left[1+\frac{2}{m+3}\cdot\frac{\alpha t}{a+\alpha t}+\frac{2\cdot 3}{m+3\cdot m+4}\left(\frac{\alpha t}{a+\alpha t}\right)^2+\dots\right]$$

The series in the brackets has the value 1 for $t=0$ and as t becomes large approaches the series

$$1+\frac{2}{m+3}+\frac{2\cdot 3}{m+3.m+4}+\ldots=S$$

If the decay curve is plotted in the usual way with $I^{-\frac{1}{2}}$ and t as coordinates it is clear that the change in slant in passing from small values of t to large values will depend upon S and will be greatest when S is greatest. The maximum deviation from linearity in the form of the decay curve which can result from absorption will therefore be produced when $m=0$, *i. e.*, when $\gamma=0$. To determine whether absorption is sufficient to account for the observed type of curve we shall therefore consider this special case for which the effect is greatest.

For $m=0$ we have

$$I=-\frac{2p\mathbf{a}}{\beta(\mathbf{a}t)^2}\int_{\mathbf{a}t}^{0}\frac{zdz}{(a+z)^2}=-\frac{2p\mathbf{a}}{\beta(\mathbf{a}t)^2}\left[-\frac{z}{a+z}+\log(a+z)\right]_{\mathbf{a}t}^{0}$$

Putting in the limits this becomes

$$I=\frac{2p\mathbf{a}}{\beta(\mathbf{a}t)^2}\left\{\log\left(1+\frac{\mathbf{a}t}{a}\right)-\frac{\frac{\mathbf{a}t}{a}}{1+\frac{\mathbf{a}t}{a}}\right\}$$

Writing θ for $\mathbf{a}t/a$

$$I=\frac{2p\mathbf{a}}{a^2\beta}\cdot\frac{1}{\theta^2}\left[\log(1+\theta)-\frac{\theta}{1+\theta}\right]$$

The curve for θ and $I^{-\frac{1}{2}}$, computed in accordance with this equation, is plotted in Fig. 188, the quantity $2p\mathbf{a}/a^2\beta$ being put equal to unity. This curve may be looked upon as showing the relation between $I^{-\frac{1}{2}}$ and t for $\mathbf{a}/a=1$. The curve for any different value of $\mathbf{a}/a$ may then be found by changing the vertical and horizontal scales to correspond to the change in $\mathbf{a}/a$.

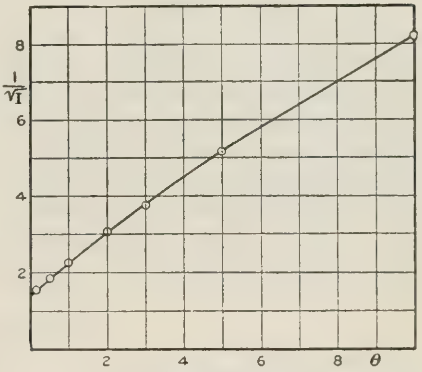

Fig. 188.

The curve of Fig. 188 is similar in form to the decay curves observed in the case of short excitation. Pierce[1] has also observed curves of nearly this form with zinc sulphide. It is possible, therefore, that the relatively slight deviation from linearity in such cases is to be ascribed to absorption. But in the case of the majority of decay curves it is clear that absorption is not to be regarded as an important factor; for no change of scale can bring about any close resemblance between the curve of Fig. 188 and the decay curves usually observed for long and moderately long excitation.

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[1] C. A. Pierce, Physical Review, xxvi, p. 314 (see Chapter VI, Fig. 77). In our own work with this same substance, "Emanations-pulver," we found a decay curve of the usual type, *i. e.*, with a well-marked "shoulder" at $t=20$ sec. (Physical Review, xxviii, p. 50, or Chapter IV, Fig. 59). It is interesting to inquire whether the difference is due to the repeated heating and cooling to which Pierce's material was subjected.

INFLUENCE OF IRREGULARITIES IN DISTRIBUTION OF THE ACTIVE MATERIAL.

Luminescent substances are in most cases solid solutions. In fact it is doubtful whether luminescence can occur in an absolutely pure substance. Pure calcium sulphide for example is not phosphorescent; but the addition of a small amount of some other metal, such as manganese or copper, gives it the power to phosphoresce brilliantly. The method of preparing the phosphorescent sulphides is such as to bring about a very intimate mixture of the constituents, and it is natural to think of the manganese, copper, or other active material as being dissolved in the sulphide.

So little is known regarding the nature of solid solutions that we can not say with certainty whether such substances are to be regarded as strictly homogeneous or not. Especially in the case of crystals it seems probable that the molecules of the solute may not be uniformly distributed throughout the mass of the solvent, but may to a greater or less extent collect in groups or minute crystals. Any lack of uniformity in the distribution of the active substance will cause a corresponding variation in the concentration of the ions produced by the exciting light; and if the nature of the solvent is such as to permit of diffusion the phenomena will be complicated by the fact that a redistribution of the ions will occur during excitation and decay. Even without diffusion, however, the form of the decay curve will be modified. For, since the rate of recombination is proportional to the square of the ionic concentration the intensity of phosphorescence will decay at different rates in different parts of the mass. The effect on the decay curve will be similar to that produced by absorption; in fact, the decay curve is modified by absorption of the exciting light only because of the resulting lack of uniformity in the ionic concentration at different depths below the surface.

Our complete ignorance of the distribution of the active material makes it almost useless to attempt any exact treatment of the problem. It is possible, however, without questionable assumptions or great analytical complexity, to predict the general character of the effect to be expected.

Let n be the number of ions per unit mass at any point; n is then some unknown function of the position of the point in question and of the time that has elapsed since the decay began. The number of recombinations per second will be αn^2 per unit volume, and the number of recombinations for the whole mass will be $\int \alpha n^2 d\tau$, where $d\tau$ is an element of volume. Disregarding the absorption of the emitted light we have

$$I = k\alpha \int n^2 d\tau$$

Since ions are destroyed only by recombination

$$\frac{dN}{dt} = -\alpha \int n^2 d\tau$$

where N is the total number of ions.

If $\bar{n}$ is the volume average of n, and $\overline{n^2}$ the volume average of n^2, so that

$$\bar{n} = \frac{1}{\tau} \int n d\tau = \frac{N}{\tau}, \quad \overline{n^2} = \frac{1}{\tau} \int n^2 d\tau, \quad \frac{dN}{dt} = -\alpha \tau \overline{n^2}$$

If we put

$$\rho = \frac{\overline{n^2}}{(\bar{n})^2}, \quad \overline{n^2} = \rho(\bar{n})^2 = \rho\frac{N^2}{\tau^2} \quad \text{and} \quad \frac{dN}{dt} = -a\tau\rho\frac{N^2}{\tau^2} = -\frac{a\rho}{\tau}N^2$$

$$\frac{1}{N} - \frac{1}{N_0} = \frac{a}{\tau}\int_0^t \rho dt$$

Writing ρ_1 for the average value of ρ between 0 and t

$$N = \frac{1}{\frac{1}{N_0} + \frac{a\rho_1}{\tau}t} \qquad I = -k\frac{dN}{dt} = \frac{ka}{\tau} \cdot \frac{\frac{d}{dt}(\rho_1 t)}{\left(\frac{1}{N_0} + \frac{a\rho_1}{\tau}t\right)^2}$$

$$\rho_1 = \frac{1}{t}\int_0^t \rho dt, \quad \frac{d}{dt}(\rho_1 t) = \rho$$

$$\therefore \frac{1}{\sqrt{I}} = \sqrt{\frac{\tau}{ka\rho}}\left(\frac{1}{N_0} + \frac{a\rho_1}{\tau}t\right)$$

Although we are unable to determine ρ and ρ_1 as functions of t it is clear that both will decrease as t increases. It is clear also that the change will become less rapid as the decay proceeds, and that both ρ and ρ_1 will sooner or latter become nearly constant. When $I^{-\frac{1}{2}}$ is plotted against t we shall therefore obtain a curve which is concave downward and which finally becomes a straight line. In other words, the decay curve will agree in form with the curves determined by experiment.

The effect upon the decay curve of an irregular distribution of the active substance may be illustrated by the following simple case: Let the active material be uniformly distributed, except that small regions occasionally occur where the concentration is abnormally large. The whole volume may thus be divided into two parts, v_1 and v_2. The distribution of the active material is uniform throughout each part, but the concentration in v_1 is different from that in v_2. When the substance is excited to phosphorescence the ionic concentration will also differ in the two regions. Let the number of ions per cubic centimeter at the end of excitation be n_1 in the volume v_1 and n_2 in the volume v_2. Throughout the region v_1 the intensity of the light emitted per cubic centimeter will be

$$i = \frac{ak}{(1/n_1 + at)^2}$$

and the *total* intensity at any instant due to this part of the whole mass will be

$$I_1 = \frac{akv_1}{(1/n_1 + at)^2}$$

The light emitted by the volume v_2 is given by the similar expression

$$I_2 = \frac{akv_2}{(1/n_2 + at)^2}$$

and the total intensity is

$$I = I_1 + I_2 = ak\left(\frac{1}{(a_1+b_1t)^2} + \frac{1}{(a_2+b_2t)^2}\right)$$

where

$$a_1 = \frac{1}{n_1\sqrt{v_1}} \qquad a_2 = \frac{1}{n_2\sqrt{v_2}} \qquad b_1 = \frac{a}{\sqrt{v_1}} \qquad b_2 = \frac{a}{\sqrt{v_2}}$$

It thus appears that the form of the decay curve is the same as though the substance possessed two bands, coincident as regards wave-length, but differing in rate of decay.

It is not at all unlikely that a condition approaching that assumed in this illustrative case actually exists in most phosphorescent substances. Upon considering the method used in preparing the phosphorescent sulphides, for example, it seems probable that the distribution of the active substance will be far from uniform. When the mixture is first prepared, and before calcination, the active material is unquestionably in the form of small discrete masses distributed irregularly through the mixture. Upon heating to redness diffusion will occur to a greater or less extent, depending upon the temperature and the duration of heating. But even at high temperatures this will be a slow process, and considerable variations in concentration are likely to remain even after prolonged heating. It is to be expected, therefore, that the phosphorescent sulphides will contain numerous nuclei of high concentration surrounded in each case by a region where the concentration is relatively small.[1]

After calcination it is often noticed also that the phosphorescence is very far from being uniform throughout the mass. Owing probably to accidental differences in concentration, or to differences in the heat treatment, the phosphorescence often differs greatly in intensity and even in color in different parts of the same mass. A phosphorescent powder made from such a mass, while presenting the appearance of homogeneity to the unaided eye, would differ greatly from point to point in the concentration of the active material.[2] Even if the mixture were so perfect that no irregularities could be detected with the microscope, a wide deviation from linearity in the decay curve is to be expected. It is a significant fact that with one exception all decay curves thus far recorded have been determined with powders prepared in practically the same way that the phosphorescent sulphides are prepared. In fact, most of the substances tested were sulphides. The exception noted above was natural willemite,[3] in which case the variation in brightness over the surface tested was plainly visible.

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[1] Since a more complete diffusion of the active material will result from prolonged heating it is to be expected, other conditions being the same, that the duration of phosphorescence will be prolonged by increasing the time of heating. This agrees with the facts observed in the preparation of the phosphorescent sulphides.

[2] While we are chiefly concerned at present with the influence of lack of homogeneity upon the decay curve, it can scarcely be doubted that the effect upon the phosphorescence spectrum is fully as important. For some reason different parts of the mass are differently affected by the process of calcination. This may be due to differences in concentration throughout the mass, or to the fact that the effect of the surrounding gas varies from point to point. When such a mass is powdered and mixed the effect is the same as though we were to make an intimate mixture of several entirely different phosphorescent substances. Each constituent has its own band or group of bands, characterized by definite wave-lengths and periods of decay, which differ according to the conditions of preparation. It is not surprising that the phosphorescence spectrum of such a material is complex; and we can scarcely expect simple laws to apply to any of the phenomena exhibited by such a mixture.

[3] The decay of phosphorescence in a specimen of willemite possessing a long-time phosphorescence has been studied by Nichols and Merritt, Physical Review, XXIII, p. 52, Fig. 53. Willemite whose phosphorescence dies out with great rapidity has been studied by Waggoner, Physical Review, XXVII, p. 209. See also Chapters, IV and VII.

It thus appears that irregularities in the distribution of the active substance are sufficient to explain the deviation from linearity in all the decay curves thus far observed. Such irregularities of distribution are not merely probable, but in many cases are perfectly obvious. But while the distribution of the active material is probably in all cases an important factor, it can not be the only factor of importance. With Balmain's paint, Pierce has found that the decay curve, which possesses the usual shoulder at ordinary temperatures, becomes almost exactly linear at a temperature of 74°,[1] while for higher temperatures it again shows a curvature of the usual kind. It appears highly improbable that such changes are brought about by temporary changes in the distribution of the active substance. Non-uniformity in the distribution of the active material also offers no explanation of the phenomena of hysteresis or of the effect of the infra-red rays.

DIFFUSION EFFECTS.

Whenever irregularities exist in the distribution of the active substance there will be a tendency for diffusion to occur. Under ordinary conditions this tendency is probably neutralized by forces which act to keep the distribution unaltered, and so long as the substance remains in the molecular form the condition is to be regarded as a stable one for the temperature and pressure at which the phosphorescent substance normally exists.

But when the material is excited to luminescence a part of the active substance will be dissociated, and since the resulting ions will possess a different mobility and will be acted upon by different forces from those that determine the behavior of the original neutral molecules, the condition of equilibrium will be destroyed, and some change in the distribution of the active substance is to be expected.

An exact discussion of the effects of diffusion would present great difficulties; for the fact that diffusion and recombination occur at the same time greatly complicates the analytical treatment. It is probable also that in crystals the diffusion constant will be different for different directions. It is clear, however, that the influence of diffusion upon the form of the decay curve must be similar to that produced by an irregular distribution of ions without diffusion. In fact, the discussion of the preceding section applies without modification to the case of substances in which diffusion of the ions may occur. Diffusion, however, will increase the rapidity with which uniformity of ionic concentration is approached during decay; and since diffusion will be most active when large concentration gradients exist, the effects of diffusion will be greatest in the early stages of decay. In cases where diffusion is an important factor we should therefore expect a sharper curvature in the early part of the curve, and a more rapid approach to linearity, than in cases where diffusion is absent.

It is not impossible that diffusion is sometimes important even when there is nearly complete uniformity in the distribution of the active substance. Owing to the absorption of the exciting light the ionization produced in the surface layer will be more intense than that produced at points beneath the surface. If the absorption is large a large gradient may thus

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[1] Physical Review, XXVI, p. 458. See also Chapter VI.

be produced in the ionic concentration, and diffusion from the surface layers inward will bring about a change in the decay curve similar in character to that caused by irregularities in the distribution of the active substance. Diffusion produced in this way would ultimately result in an appreciable diminution in the surface concentration of the active material, and we should therefore expect that the intensity of luminescence would be diminished in such a substance by prolonged excitation. No effect of this kind has been observed by us in the case of Sidot blende, but the observations of Werner[1] with a SrZn compound show evidence of fatigue resulting from prolonged excitation.

The change in the form of the decay curve due to changes in the duration of excitation may be explained, at least in a general way, as a result of diffusion. Diffusion of the ions will occur during excitation as well as during decay. After prolonged excitation, therefore, the volume occupied by ions will be greater than after short excitation, and the rate of decay—in other words the slant of the decay curve—will be correspondingly reduced.[2]

Diffusion also offers an explanation of the phenomena of hysteresis in phosphorescent substances. After prolonged excitation and subsequent decay the neutral molecules that result from recombination will be distributed through a larger volume than before. Since the original distribution of the active material was a stable one there will be a gradual return to the normal distribution. But this will be a slow process and may well require several days for its completion. In the mean time the material is in such a condition that the decay following renewed excitation will be more gradual than the normal, even for a short excitation. The spreading out of the active substance by diffusion, which would normally require a long excitation, has already been accomplished by the preceding excitation, whose effects have not yet disappeared. Hysteresis effects such as those discussed in Chapter IV are therefore to be expected.

If this explanation of hysteresis is correct the effect of the infra-red rays must be to facilitate the return of the substance to its normal condition; in other words, to increase the rapidity of the diffusion by which the original distribution of the active material is restored. It is natural to expect such an effect in substances which are able to absorb the infra-red rays. But if the restoration is accomplished by the diffusion of neutral ions the rapidity of the action is surprising, for with strong infra-red rays we have found that an exposure of only a few seconds is sufficient to restore Sidot blende to its standard condition.[3]

INFLUENCE OF IONIC GROUPING.

In discussing thermo-luminescence and the effect of infra-red rays upon phosphorescence Wiedemann and Schmidt[4] have suggested that some of the ions produced during excitation form semi-stable combinations or

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[1] A. Werner, Ann. der Phys., 24, p. 164, 1907.

[2] If the volume occupied by ions is v_1 for short excitation and v_2 for long excitation, the ionic concentrations will be n/v_1 and n/v_2 respectively, and the two intensities of phosphorescence will be proportional, to an^2/v_1 and $an/^2/v_2$. Prolonged excitation therefore produces an effect which is equivalent to a diminution in the coefficient of recombination.

[3] See Chapter V.

[4] Ann. der Phys., 56, p. 247, 1895.

groups with the neutral molecules of the solvent, and that these groups may afterwards be broken down, and the ions liberated, by rise in temperature or by the absorption of infra-red rays. The formation of such groups as the result of ionization seems extremely probable, especially in the case of solids, and can scarcely fail to be of importance in any satisfactory theory of phosphorescence. Introducing such additional hypotheses as are necessary to give definiteness to the suggestion of Wiedemann and Schmidt, let us consider what the influence of such ionic groups will probably be.

We shall assume that the first effect of the exciting light is to produce dissociation in a part of the active material. The dissociation assumed may be either chemical or electrolytic[1] and if of the latter type it may either be similar to the dissociation of ordinary electrolysis, or may consist of the expulsion from the molecule of one or more electrons, and thus resemble more closely the ionization of a gas by X-rays. For the sake of definiteness we shall assume that the effect of the exciting light is to produce such violent vibrations as to liberate a single electron from the molecule.

The two ions produced in this type of dissociation will differ greatly in mobility. The negative ion, owing to its small mass, will possess a velocity hundreds of times greater than that of the heavy positive ion, and in consequence will move about in the substance with considerable freedom. While the electrons will at times attach themselves to the molecules of the solid solvent this condition will usually be only temporary. We may assume in general that a constant fraction of the whole number of negative ions consists of electrons that are moving freely. The positive ions on the other hand will possess only a small mobility. While some of these ions will remain free, it is to be expected that many will attach themselves to molecules of the solvent or to undissociated molecules of the active substance. It is to be noted that the small velocity of the positive ions makes it probable that the groups formed by the union of a positive ion with a neutral molecule will be more permanent than similar groups formed by the negative ion!

The collisions between positive and negative ions, which lead to the more or less gradual decay of the ionized condition after the exciting light has ceased to act, will be of three different kinds: (1) collisions between a negative ion and a free positive ion; (2) collisions between a negative ion and a positive ion that has attached itself to a neutral molecule of the solvent, and (3) collisions between a negative ion and a positive ion that is attached to a neutral molecule of the active substance. The number of modes of recombination may in fact be greater than three, since the positive ion may become the nucleus of more complicated molecular groups. But we shall restrict the discussion to cases in which there are three modes of recombination.

When recombination occurs it is to be expected that vibrations will be set up in the resulting neutral molecule, and these vibrations, in the theory here considered, are assumed to be the source of the light emitted during the phosphorescence. But the vibrations corresponding to the different

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[1] Since the electro-magnetic disturbance that constitutes light can get a hold on the molecules of the active material only by exerting forces upon the electrical charges in the molecule, and will always tend to separate the positive and negative parts, it appears probable that the first effect of the exciting light is always to produce some type of electrolytic dissociation, and that any chemical changes which may be exhibited are secondary effects.

modes of recombination will probably differ in violence, in frequency, and in radiating power.

Of the total number n of positive ions at any time t let φn be free, and ψn attached to neutral molecules of the active substance; then $(1-\varphi-\psi)n$ will be attached to molecules of the solvent. φ and ψ are proper fractions whose sum is less than unity, and which, in general, are functions of t; for the distribution of the positive ions will be subject to alteration during the decay of phosphorescence as well as during excitation. The number of recombinations between a free positive ion and an electron in unit time will be proportional to the number of free positive ions φn, and to the number of free negative ions n, and may therefore be put equal to $\alpha_1\varphi n^2$, where α_1 is the coefficient of recombination. If the energy radiated as light due to one recombination is p_1 the intensity of the phosphorescence due to this mode of recombination will be

$$I_1=p_1\alpha_1\varphi n^2$$

Similarly

$$I_2=p_2\alpha_2\psi n^2 \qquad I_3=p_3\alpha_3(1-\varphi-\psi)n^2$$

for the other two types of recombination.

The total phosphorescent light will thus consist of three parts. If the different modes of recombination give rise to vibrations of different frequency the phosphorescence spectrum will consist of three bands which decay at different rates, and which may differ widely in intensity.

The determination of the law of decay of phosphorescence upon the basis of the theory just outlined is thus seen to involve the determination of n, φ, and ψ as functions of t. In the general case the solution presents difficulties that are wellnigh insurmountable. The problem may be simplified, however, by an assumption which, while doubtless not exactly true, probably gives in the majority of cases a close approximation to the actual conditions. It is assumed, namely, that $\alpha_1=\alpha_2=\alpha_3$; in other words, the probability that a collision will result in recombination is the same for the three types of collision. In this case

$$(1)\qquad \frac{dn}{dt}=-\alpha\varphi n^2-\alpha\psi n^2-\alpha(1-\varphi-\psi)n^2=-\alpha n^2$$

$$(2)\qquad n=\frac{1}{1/n_0+\alpha t}$$

where n_0 is the number of positive (or negative) ions when excitation ceases.

To determine φ and ψ as functions of t it is necessary to make some assumption regarding the rate at which the free positive ions attach themselves to neutral molecules. Since the number of neutral molecules is presumably large as compared with the number of ions, it is reasonable to assume that the rate at which new groups are formed is proportional to the number of ions that are still free to enter into such combination. In other words, we may assume $k_1\varphi n$ and $k_2\varphi n$ as the rates of formation of new groups of the two possible types. Since the positive ions, whether free or attached, are also recombining with the negative ions we have

$$(3)\qquad \frac{d}{dt}(\varphi n)=-\alpha\varphi n^2-(k_1+k_2)\varphi n$$

While positive ions will occasionally break loose from the groups to which they have attached themselves and return to the "free" condition, this will occur only rarely on account of the sluggishness with which these ions move. The small positive term due to this cause which should appear in the right hand member of equation (3) is therefore negligible and may be omitted. At high temperatures, however, and perhaps under other special conditions, the omission of this term will no longer be permissible. If the molecular movements are sufficiently violent, due to high temperature or other causes, the formation of groups may even be prevented altogether. Such cases will be considered later.

Equation (3) may be written

$$\frac{d}{dt}(\varphi n)=\varphi\frac{dn}{dt}+n\frac{d\varphi}{dt}=-\alpha\varphi n^2-(k_1+k_2)\varphi n$$

Remembering that $dn/dt=-\alpha n^2$ this becomes

$$\frac{d\varphi}{dt}=-(k_1+k_2)\varphi \qquad\qquad \varphi=\varphi_0 e^{-mt}$$

where $m=k_1+k_2$ and φ_0 is the value of φ for $t=0$.

In the case of the positive ions that are attached to neutral molecules of the active substance recombinations are occurring with negative ions at the rate $\alpha\psi n^2$, while new groups are being formed by the attachment of free positive ions at the rate $k_1\varphi n$

$$\therefore \frac{d}{dt}(\psi n)=-\alpha\psi n^2+k_1\varphi n$$

or

$$(5) \qquad \psi\frac{dn}{dt}+n\frac{d\psi}{dt}=-\alpha\psi n^2+k_1\varphi n$$

Since

$$\frac{dn}{dt}=-\alpha n^2$$

we have

$$\frac{d\psi}{dt}=k_1\varphi=k_1\varphi_0 e^{-mt} \qquad\qquad \therefore \psi=-\frac{k_1\varphi_0}{m}e^{-mt}+\text{const.}$$

Putting ψ_0 for the value of ψ when $t=0$

$$(6) \qquad \psi=\psi_0+\frac{k_1\varphi_0}{m}(1-e^{-mt})$$

For the intensities of the three constituents of the phosphorescent light we have therefore

$$I_1=p_1\alpha\varphi n^2=\frac{p_1\alpha\varphi_0 e^{-mt}}{(1/n_0+\alpha t)^2}$$

$$I_2=p_2\alpha\psi n^2=\frac{p_2\alpha[\psi_0+k_1\varphi_0/m(1-e^{-mt})]}{(1/n_0+\alpha t)^2}$$

$$I_3=p_3\alpha(1-\varphi-\psi)n^2=\frac{p_3\alpha[1-\psi_0-k_1\varphi_0/m-k_2\varphi_0/m\cdot e^{-mt})]}{(1/n_0+\alpha t)^2}$$

Since we have usually plotted the reciprocal square root of the intensity of phosphorescence, it will be convenient to use the same procedure here.

$$1/\sqrt{I_1} = \frac{1}{\sqrt{p_1\alpha\varphi_0}}\, e^{\frac{1}{2}mt}(1/n_0+\alpha t)$$

$$1/\sqrt{I_2} = \frac{1/n_0+\alpha t}{\sqrt{p_2\alpha[\psi_0+k_1\varphi_0/m(1-e^{-mt})]}}$$

$$1/\sqrt{I_3} = \frac{1/n_0+\alpha t}{\sqrt{p\alpha[1-\psi_0-k_1\varphi_0/m-k\varphi_0/m\cdot e^{-mt}]}}$$

Replacing certain groups of constant terms by single letters for brevity, these expressions may be written

$$1/\sqrt{I_1} = A_1\epsilon^{\frac{1}{2}mt}(1/n_0+\alpha t)$$

$$1/\sqrt{I_2} = \frac{1/n_0+\alpha t}{\sqrt{A_2-B_2e^{-mt}}}$$

$$1/\sqrt{I_3} = \frac{1/n_0+\alpha t}{\sqrt{A_3-B_3e^{-mt}}}$$

If a curve is plotted for $1/\sqrt{I_1}$ in accordance with the above equation it is found to be of the type shown in Fig. 190 for $\gamma=0$. The curve for $1/\sqrt{I_2}$ and $1/\sqrt{I_2}$ is concave *upward* during the early stages of decay, becoming practically straight when t is so large as to make e^{-mt} inappreciable.

No decay curves corresponding to either of these types has been observed. It must be remembered, however, that the effects of absorption, diffusion, and irregular distribution have been neglected in the present discussion. It is probable that one or more of these sources of disturbance are present, in which case the theoretical decay curves would be modified in such a way as to make them correspond more nearly with the curves actually observed. If m is large, for example, the curve for $I_2^{-\frac{1}{2}}$ will be straight except in the immediate neighborhood of $t=0$. Irregularities in the distribution of the active substance would then produce a deviation from linearity, as previously discussed. It appears probable that the observed facts, in the cases of phosphorescence thus far studied, are best explained in this way. It is interesting to note, however, that curves may be obtained as the result of ionic grouping which agree very closely with the experimental curves, even on the assumption of a uniform distribution of the active material. If, for example, I_1 and I_2 *both* contribute to the phosphorescence, while I_3 is zero or negligible

$$I = I_1+I_2 = \frac{p_2\alpha[\psi_0+k_1\varphi_0/m\cdot(1-e^{-mt})]+p_1\alpha\varphi_0e^{-mt}}{(1/n_0+\alpha t)^2}$$

$$1/\sqrt{I} = \frac{1/n_0+\alpha t}{\sqrt{A+Be^{-mt}}} \qquad (7)$$

where

$$A = p_2\alpha\left(\psi_0+\frac{k_1\varphi_0}{m}\right) \qquad B = p_1\alpha\varphi_0-p_2\alpha\frac{k_1\varphi_0}{m}$$

In case all three modes of recombination contribute to the phosphorescence we obtain a similar expression for $I^{-\frac{1}{2}}$, except that A and B now have the values

$$A = p_2 a\left(\varphi_0 + \frac{k_1\varphi_0}{m}\right) + p_1 a\left(1 - \varphi_0 - \frac{k_1\varphi_0}{m}\right)$$

$$B = p_1 a\varphi_0 - p_2 a\frac{k_1\varphi_0}{m} - p_3 a\frac{k_2\varphi_0}{m}$$

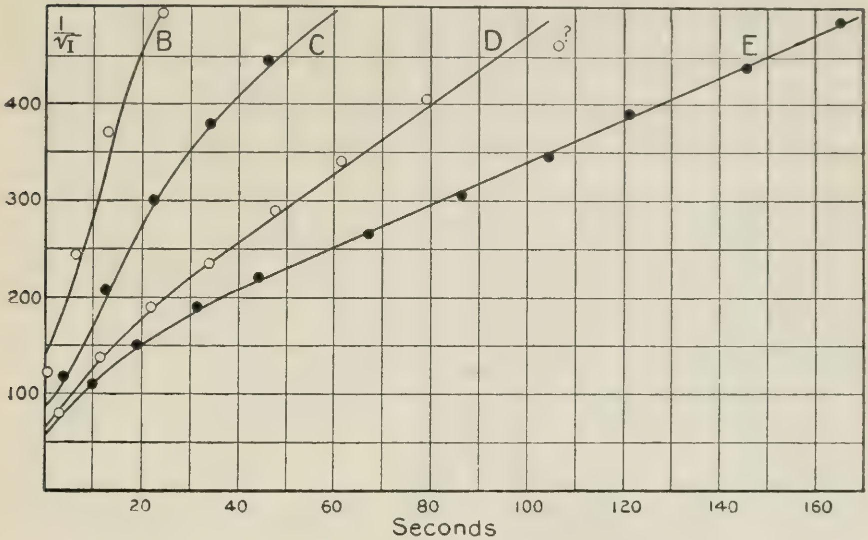

Fig. 189.

Observed decay curves for different durations of excitation compared with curves computed from the equation

$$\frac{1}{\sqrt{I}} = \frac{1/n_1 + at}{\sqrt{B(\gamma + e^{-mt})}}$$

The times of excitation and the relative numerical values of the constants used in computation are as follows:

Curve.	Excitation.	γ	1/No	$\sqrt{B}$	
E	60 sec.	0.36	72	1	
D	37	0.4	167	2.18	$a = 4.8$
C	11.6	0.1	336	4	$m = 0.16$
B	5.4	0.1	650	4.35	

In Fig. 189 several curves have been plotted for $I^{-\frac{1}{2}}$ by means of this equation. Values of the constants have been determined by trial so as to make these curves correspond as nearly as possible with the series of experimental curves obtained with Sidot blende by varying the time of excitation.[1] Observational points are indicated by circles. It will be seen that, except in the case of one point on curve *D*, the agreement is highly satisfactory.

To give an idea of the character of the decay curves which might result from the presence of grouped ions (disturbances due to diffusion, absorption, etc., being neglected) we may write equation (7) in the form

$$\frac{1}{\sqrt{I}} = \frac{1/n_0 + at}{\sqrt{B}} \cdot \frac{1}{\sqrt{\gamma + e^{-mt}}} = \frac{(1/n_0 + at)}{\sqrt{B}} T$$

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[1] Nichols and Merritt, Physical Review, XXIII, p. 45. See also Chapter IV.

where

$$T=\frac{1}{\sqrt{\gamma+e^{-mt}}} \quad \text{and} \quad \gamma=A/B$$

The first factor alone plots as a straight line. The deviation from linearity in the curve for $I^{-\frac{1}{2}}$ is therefore determined by the second factor T. Putting $m=1$ we have computed T as a function of t for several values of γ, the results being plotted in Fig. 190. For values of γ ranging from 0.1 to 0.5 the curves are of such a character as to correspond with the experimental curves for $I^{-\frac{1}{2}}$. But for smaller values of γ a double curvature is shown which is not found in any of the curves that we have determined. There is, however, an indication of such a double curvature in some of the results of Pierce. It is clear that disturbances, due, for example, to irregularities in the distribution of the active material, might so alter the early part of the curve as to eliminate any peculiarities of this nature. In fact, there is at present so much uncertainty regarding the relative importance of the different factors that influence the form of the curve for small values of t that it is difficult to reach any definite conclusions concerning this part of the curve. Experiments bearing upon the distribution of the active material, the rate of diffusion of the ions, and related matters are greatly needed.

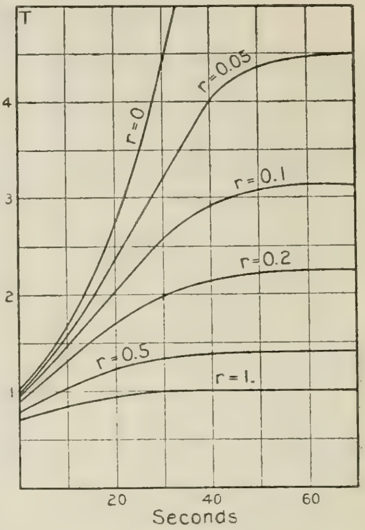

Fig. 190.

Curves showing relation between T and t for different values of γ where

$$T=\frac{1}{\sqrt{\gamma+e^{-t}}}$$

HYSTERESIS, TEMPERATURE EFFECTS, ETC., EXPLAINED BY IONIC GROUPING.

To account for the hysteresis exhibited by phosphorescent substances, in other words, the effect of a previous exposure upon the phosphorescence produced by a given excitation, it is necessary to consider the essential difference that probably exists between the groups formed by the union of positive ions with neutral molecules of the active substance and those formed by the attachment of positive ions with molecules of the solvent. For the sake of brevity, as well as for the reasons that will appear shortly, we shall refer to the former as *favorable groups* and to the latter as *unfavorable groups.*

We have already introduced the assumption that light is produced by the recombination of a negative ion with a favorable group, while the recombination of the unfavorable groups, at least in some cases, gives out no light. A difference is to be expected also in the behavior of the neutral molecules that result from recombination in the two cases. A favorable group consists in a positive ion attached to at least one neutral molecule *of the same sort.* It seems natural to expect that forces similar to those that hold together the molecules of a crystal may cause this grouping to persist even after recombination has occurred. In the case of the unfavorable groups this tendency to persist can scarcely be present in the same degree if at all.

The condition of the phosphorescent substance is thus different after phosphorescence has ceased from what it was before excitation. The difference consists in the presence in the mass of a larger number of grouped molecules of the active substance, which are so intimately connected that when one member of the group is dissociated during subsequent excitation its positive ion is in a position to form immediately one of the groups favorable to phosphorescence. After the substance has been excited it is therefore in a condition which enables a subsequent excitation to produce a larger proportion of favorable groups than would be produced by a similar excitation of the fresh substance. In other words, the ψ_0 of equation (7) is increased.

During excitation we have dissociation and recombination taking place at the same time; and the recombinations that occur during excitation will bring about the same change in the condition of the substance that we have assumed during decay. The value of ψ_0 will therefore increase with the duration of exposure to the exciting rays. Prolonged excitation, up to the point where saturation is reached, also increases the number of ions, *i.e.*, the value of n_0. A series of decay curves for different times of exposure should therefore resemble the curves of Fig. 189, which are computed from equation (7) by giving progressively increasing values to the constants ψ_0 and n_0.

The new condition in which a substance is left after phosphorescence can scarcely be one of complete stability. The natural and stable arrangement of the molecules is that of the substance before it has been disturbed by the action of light. It is to be expected, therefore, that there will be a more or less gradual return to the normal state after the light has ceased to act. The recombination of the ions produced by excitation, with the accompanying phosphorescence, forms only one stage in the complete return to the normal state, and is followed by a more gradual breaking down of the molecular groups resulting from recombination. We thus have an explanation of the effect of rest. The effect of exposure to infra-red rays and of elevation of temperature is to hasten the return to the normal state by increasing the rate at which these groups disintegrate.

To account for the action of the infra-red rays during excitation and decay it is only necessary to assume that these rays also have the power of breaking down the "favorable groups." In the case of Sidot blende the effect on the unfavorable groups appears to be inappreciable. Upon exposure to infra-red during decay the first result is to diminish the number of favorable groups, and to correspondingly increase the number of free positive ions. This, by itself, will not greatly alter the intensity of phosphorescence; for in the phosphorescence of Sidot blende the recombination of a free positive ion appears to be nearly or quite as effective as the recombination of a favorable group. But an increase in the number of free ions causes an increase in the rate at which unfavorable groups are formed. The positive ions that are shaken loose from the favorable groups therefore pass quickly into the inactive condition, and a rapid diminution in the intensity of phosphorescence results. The rate of decrease of course depends upon the intensity of the active rays.

If the infra-red rays are allowed to act for a short time and are then cut off, the condition of the phosphorescent substance will differ in two respects from that which it would have reached during ordinary decay: (1) the number of favorable groups is less than it would have been without the action of the longer waves; (2) the number of free ions is, at least to some extent, in excess of the normal. After the infra-red rays have ceased to act, however, the free ions will soon form groups again, either favorable or unfavorable, and the decay curve will quickly return to the standard form. But the number of favorable groups will be less than if the infra-red rays had not acted. The effect of exposure to the longer waves is simply to bring the substance quickly into the same condition that it would ordinarily acquire only after a much longer period of decay. The theory here discussed is thus seen to be in agreement with the experimental results recorded in Chapter V.

It seems probable that in some substances certain rays, presumably in the infra-red, may have the effect of breaking down the unfavorable as well as the favorable groups. In such cases exposure to these rays would probably bring about an increase in the brilliancy of phosphorescence instead of a decrease. This is the case with certain of the phosphorescent sulphides. The same effect would be produced in substances where the recombination of a free positive ion gives out more light than that of an attached ion, *i. e.*, where $p_1 > p_2$.

In cases like that of Sidot blende the form of the decay curve as modified by exposure to infra-red rays may be determined as follows:

We shall assume that the rate at which favorable groups are broken down is proportional to the intensity of the active rays I_r and the number of favorable groups present (ψn). We therefore have

$$(8) \qquad \frac{d}{dt}(\psi n) = -a\psi n^2 - R\psi n - k_1\varphi n$$

where R is proportional to I_r.

The destructive effect of the infra-red is so great, even for rays of small intensity, while k_1 is so small, that the last term $k_1\varphi n$ may in general be neglected. It is only in the case of exposure to very weak rays, or with substances which show the infra-red effect in small intensity, that the omission of this term will lead to appreciable errors. Equation (8) therefore becomes

$$\psi\frac{dn}{dt} + n\frac{d\psi}{dt} = -a\psi n^2 + n\frac{d\psi}{dt} = -a\psi n^2 - R\psi n \qquad \frac{d\psi}{dn} = -R\psi$$

$$(9) \qquad \psi = \psi_1\epsilon^{-Rt}$$

where t is reckoned from the time when exposure to the infra-red rays begins. If we take t as the time that has elapsed since the end of excitation we have

$$\psi = \psi_1 e^{-R(t-t_1)}$$

where t_1 is the time at which the longer waves begin to act and ψ_1 is the value of ψ at this time.

To determine the number of free positive ions φn after the infra-red rays begin to act we have the equation

$$\frac{d}{dt}(\varphi n) = -\alpha\varphi n^2 + R\psi n - k_2\varphi n$$

$$\varphi\frac{dn}{dt} + n\frac{d\varphi}{dt} = -\varphi\alpha n^2 + n\frac{d\varphi}{dt} = -\alpha\varphi n^2 + R\psi n - k_2\varphi n$$

$$\frac{d\varphi}{dt} + k_2\varphi = R\psi = R\psi_1 e^{-R(t-t_1)}$$

$$\text{(10)} \qquad \varphi = \varphi_1 c^{-k_2(t-t_1)} + \frac{R\psi_1}{k_2 - R} e^{-R(t-t_1)}$$

An interesting special case, corresponding to the experimental conditions in much of our work with Sidot blende, is that in which the exposure to infra-red rays begins at once when excitation ceases, *i. e.*, $t_1 = 0$. In this case

$$\varphi_1 = \varphi_0 \quad \psi_1 = \psi_0 \quad \varphi = \varphi_0 e^{-k_2 t} + \frac{R\psi_0}{k_2 - R}(e^{-Rt} - e^{-k_2 t}) \quad \psi = \psi_0 e^{-Rt}$$

$$I = p_1\alpha\varphi n^2 + p_2\alpha_2\psi n^2 = (A_1 e^{-Rt} + B_1 e^{-k_2 t})n^2$$

where

$$A_1 = p_2\alpha_2\psi_0\frac{k_2}{k_2 - R} \qquad B_1 = p_1\alpha_1\left(\varphi_0 - \frac{R\psi_0}{k_2 - R}\right)$$

For the special case where $p_1\alpha_1 = p_2\alpha_2$,

$$\frac{1}{\sqrt{I}} = \eta = \frac{1/n_0 + \alpha t}{\sqrt{\frac{\psi_0 k_2}{k_2 - R}\epsilon^{-Rt} + \left(\varphi_0 - \frac{R\psi_0}{k_2 - R}\right)e^{-k_2 t}}}$$

If the infra-red rays are intense so that R/k_2 is large

$$\frac{1}{\sqrt{I}} = \frac{1/n_0 + \alpha t}{\sqrt{k_2\psi_0/R \cdot e^{-Rt} + (\psi_1 + \psi_0)e^{-k_2 t}}}$$

and in the extreme case where R may be treated as infinite

$$\frac{1}{\sqrt{I}} = \frac{1/n_0 + \alpha t}{\sqrt{(\varphi_0 + \psi_0)e^{-k_2 t}}}$$

This gives a curve having the same form as the observational curve shown in Fig. 72. The data of Fig. 70 will be found to give a curve of the same form for $1/\sqrt{I'}$, but the curve has been plotted only in the case of Fig. 72.

At high temperatures the increased activity of the molecular movements will tend to prevent the formation of groups, or rather to destroy the groups almost as quickly as they are formed. All those phenomena that depend upon the existence of groups will therefore become less prominent as the temperature rises. Sooner or later a temperature will be reached where groups can no longer exist. At temperatures above this point we should expect no effect from exposure to the infra-red, and all hysteresis effects should disappear. The experiments of Pierce show that hysteresis still persists in Balmain's paint at 133° C. No other data bearing upon this point are available.

It would be a matter of no great difficulty to develop the theory of ionic groups in much greater detail than has here been attempted, for when uncomplicated by the effects of irregular distribution and diffusion the theory lends itself readily to analytical treatment. But in view of the small amount of experimental data that are available for testing the conclusions it seems inadvisable to carry the development further at present.

SUMMARY.

In the case of a homogeneous substance having only one band in its phosphorescence spectrum and uniformly excited throughout, the dissociation theory first suggested by Wiedemann and Schmidt leads to a linear relation between t and $I^{-\frac{1}{2}}$ during the decay of phosphorescence. The observed decay curve, however—*i. e.*, the curve obtained when $I^{-\frac{1}{2}}$ is plotted as a function of t—usually shows a more or less sharp curvature in the early stages of decay, and only later becomes straight. Using the dissociation theory as a basis, we have discussed first the influence upon the decay curve of various disturbing factors, such as absorption of the exciting and emitted light, diffusion, etc. We have then considered the effect upon the various phenomena of phosphorescence of the formation of complex ions, which are assumed to be produced by the attachment of simple ions to neutral molecules; and after the introduction of certain hypotheses regarding the behavior of such ionic groups, an analytical theory is developed.

Briefly the results of the discussion are as follows:

While the observations thus far made on the decay of phosphorescence are perhaps not sufficient to definitely disprove Becquerel's explanation of the form of the decay curve, viz, that the curvature is due to the existence of two bands in the phosphorescence spectrum, numerous objections to this explanation are discussed. For example, the fact that the decay curve has the usual form even when precautions are taken to study only a single band; that the phosphorescence spectrum remains unaltered during decay; the fact that the decay curve is of the same type for all substances thus far studied; and the fact that Becquerel's explanation takes no account of hysteresis phenomena, the effect of infra-red rays, etc.

2. It is shown that lack of transparency in the phosphorescent substance, resulting in the absorption of either the exciting light or the emitted light or both, will cause a slight curvature in the decay curve. But the effect can under no circumstances be sufficient to account for the observed deviation from linearity.

3. Lack of uniformity in the distribution of the active material throughout the mass of the phosphorescent substance will cause a deviation from linearity corresponding to that actually observed. Under certain con-

ditions the effect is the same as though the substance possessed two or more bands, coincident as regards wave-length, but differing in rate of decay. It is pointed out that such a lack of homogeneity is to be expected from the method of preparation of phosphorescent substances, and has a great deal to do with the complexity of the phenomena.

4. Diffusion of the ions will produce effects similar to those caused by irregularities in the distribution of the active material without diffusion, but the effects will be more marked. An explanation of hysteresis effects may also be based upon the presence of diffusion.

5. The assumption of complex or grouped ions is shown to lead to a law of decay which agrees closely with experiment. Ionic grouping also accounts satisfactorily for the dependence of the decay curve upon the duration of excitation and the previous history of the substance, and for the effect of exposure to the infra-red.

The preceding discussion appears to justify the conclusion that the dissociation theory proposed by Wiedemann and Schmidt accounts satisfactorily for all the phenomena of phosphorescence thus far studied. Additional quantitative data are greatly needed, however, in order to make possible the further development of the theory. The present difficulty is not so much in accounting for the observed facts as in discriminating between different hypotheses that are at present equally plausible, and in deciding to what extent various recognized sources of disturbance are of importance. The form of the decay curve, for example, may be accounted for equally well by the assumption of two bands, by an irregular distribution of the active substance, by diffusion, or by ionic grouping, and is unquestionably modified by absorption. No quantitative test of either explanation is possible until the relative importance of the other factors is known. It may be, for instance, that diffusion does not occur at all; and it is possible, but not probable, that the disturbances due to lack of homogeneity are of no significance. Experiments that will furnish a definite answer to questions of this sort are of the greatest importance in the development of this or any other theory of phosphorescence.

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